HEAT AND THERMODYNAMICS

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CHAPTER OVERVIEW

1: Introductory Remarks

1.1: Introduction

Thermodynamics is a subject that has a wide variety of applications, including many in practical and engineering contexts. However, by choice, I shall be treating this subject from a very “academic” point of view, in which disembodied forces will compress ideal gases with frictionless pistons, seemingly far removed from the real engines of steel and gasoline which engineers must design. This approach may appeal to those with an academic bent – but is it likely to be useful to the aspiring engineer who lives and works in the real world? Need the practical engineer know and understand all this airy-fairy mumbo-jumbo? I would just argue this – that the “academic” approach deals with the *fundamental physical principles* upon which all practical applications must be built, and that an engineer above all others must thoroughly understand these principles. The fundamental principles do not cease to apply in the practical world!

I don’t expect to get down to serious thermodynamics in the opening chapter. Instead I shall just discuss a few isolated, unrelated miscellaneous bits and pieces that I thought worth doing. Furthermore, anyone who opens a book on thermodynamics will see the symbol ∂ liberally sprinkled over almost every page, so I thought I’d write a short chapter – Chapter 2 - on partial derivatives. That will not be intended as a formal course in mathematics, but just a brief summary of the main properties of partial derivatives that you are likely to need. Thus I shan’t get down to serious thermodynamics until Chapter 3.

1.2: Caloric, Calories, Heat and Energy

It has long been understood that heat is a form of energy. But this has not always been so, and indeed it was not generally accepted until the middle of the nineteenth century. Before then, heat was treated as though it were some sort of “imponderable (weightless) fluid” known as caloric, which could flow out of one body into another. It is true that as long ago as 1799 Humphrey Davy showed that ice could be melted merely by rubbing two pieces together without the need of any “caloric”, and indeed this could not be explained by the “caloric” theory. Davy argued – quite correctly – that friction between two bodies must generate “a motion or vibration of the corpuscles of bodies”, and that the observation of the melting of ice by rubbing alone showed that “we may reasonably conclude that this motion or vibration is heat”. Likewise at about the same time Benjamin Thompson, Count Rumford, showed that the boring of cannon continuously produced heat in proportion to the amount of work done in the boring process, and the amount of heat that could be so produced was apparently inexhaustible. This again should have sounded the death knell of the caloric theory, and, like Davy, Rumford correctly suggested that heat is a form of motion.

In spite of this evidence and the arguments of Davy and Rumford, it wasn’t until the middle of the nineteenth century that caloric theory finally died, and this was a result of the famous experiments of James Prescott Joule to determine the mechanical equivalent of heat.

There is some question as to whether the name should be pronounced “jool” (to rhyme with fool) or “jowl” (to rhyme with fowl). Joule was from a beer-brewing family in Manchester, in the North of England. In a north of England accent, “jowl” would be a preferred pronunciation, while “jool” would come more naturally in the south of England, although most modern Mancunians, like the rest of us, nowadays say “jool”. The uncertainty in the pronunciation is an old one, and was used by the brewery (which no longer exists) in Joule’s day as an advertising slogan for the beer. I am indebted to Dr Graham McDonald of the Joule Laboratory, Salford University, who found the actual advertising slogan for Joule’s Ales:

> Do you pronounce it Joule’s to rhyme with Schools, Joule’s to rhyme with Bowls, or Joule’s to rhyme with Scowls? Whatever you call it, by Joule’s, or Joule’s, or Joule’s. It’s GOOD!

In the nineteenth century (and continuing to today) the metric unit of heat was the *calorie* (the quantity of heat required to raise the temperature of a gram of water through one Celsius degree), and the imperial unit was the *British Thermal Unit* (the quantity of heat required to raise the temperature of a pound of water through one Fahrenheit degree). What Joule did was to show that the expenditure of a carefully measured amount of work always produced the same carefully measured amount of heat. He did this by using falling weights to drive a set of rotating paddles to stir up a quantity of water in a calorimeter, the motion (kinetic energy) of the water being damped by a system of fixed vanes inside the calorimeter. The amount of energy expended was determined by the loss of potential energy of the falling weights, and the amount of heat generated was determined by the rise in temperature of the water. He deduced that the “mechanical equivalent of heat” is 772 foot-pounds per British thermal unit. That is, 772 foot-pounds of work will raise the temperature of a pound of water through one Fahrenheit degree. In more familiar metric units, the mechanical equivalent of heat is 4.2 joules per calorie. He wrote: “If my views be correct,... the temperature of the river Niagara will be raised about one fifth of a degree by its fall of 160 feet.”

(*Exercise*: Verify this by calculation or by measurement, whichever you find more convenient.)

Once we have accepted that heat is but a form of energy, there should be no further need for separate units, and the joule will serve for both. That being so, we can interpret Joule’s experiment not so much as determining the “mechanical equivalent of heat”, but rather as a measurement of the specific heat capacity of water.

In spite of this, the calorie is still (regrettably) used extensively today. Part of the reason for this is that, in measuring heat capacities, we often drop a hot sample into water and measure the rise in temperature of the water. This tells us rather directly what the heat capacity of the sample is in calories – i.e. the heat capacity relative to that of water. I suspect, however, that the calorie remains with us not for scientific reasons, but because old habits die hard. There are several problems associated with the continued use of the calorie. Roughly, the calorie is the heat required to raise the temperature of a gram of water through 1 C$^{\text{o}}$. For precise work, however, it becomes necessary to state not only the isotopic constitution (and the purity) of the water, but also through which Celsius degree its temperature is raised. Thus in the past we have defined the calorie as “one hundredth of the heat required to raise the temperature of a gram of water from 0$^{\text{o}}$C to 100$^{\text{o}}$C”; or again as “the heat required to raise the temperature of a gram of water from 14.5$^{\text{o}}$C to 15.5$^{\text{o}}$C”. This latter is about 4.184 joules, but there is really no need to know this conversion factor, unless you are specially interested in the specific heat capacity of water (which, by the way is rather larger than many common substances). (You may have noticed that I have sometimes written ^{o}C and sometimes C^{o}, and you may have wondered which is correct, or whether the degree symbol should be used at all. This will be discussed in Chapter 3.)

The "calories" that nutritionists quote when talking about the calorific value of foods, is actually the kilocalorie and it is sometimes (but by no means always) written Calorie, with a capital C. How much simpler it would all be if all of us just used joules!

There is yet another problem associated with the continued use of "calories". That is that we often come across formulas and equations in thermodynamics in which a mysterious factor "*J*" appears. For example, there is a well-known equation $C_P - C_V = R/J$. This relates the specific heat capacities of an ideal gas at constant pressure and volume to the universal gas constant R. It is supposed to be understood in the equation that C_P and C_V are to be expressed in calories and R is to be expressed in joules. The conversion factor between the two units, J, is the mechanical equivalent of heat, or the number of joules in a calorie. This conversion factor between units will not be used in these notes, and all quantities expressing heat of energy will be measured in the same units, which will normally be joules. The equation quoted above will be rendered simply as $C_P - C_V = R$. (The letter J, not in italics, will, of course, continue to be used to denote the unit the joule, but not J, in italics, for a conversion factor.)

1.3: Extensive and Intensive Quantities

There is a useful and important distinction in thermodynamics between extensive (or "capacitive") and *intensive* quantities.

Extensive quantities are those that depend upon the amount of material. Examples would include the volume, or the heat capacity of a body. The *heat capacity* of a *body* is the amount of heat required to raise its temperature by one degree, and might be expressed in J $\text{C}^{\text{o}-1}$.

Intensive quantities do not depend on the amount of material. Temperature and pressure are examples. Another would be the *specific heat capacity* of a *substance*, which is the amount of heat required to raise unit mass of it through one degree, and it might be expressed in J kg^{-1} $\text{C}^{\text{o}\,-1}$. This is what is commonly (though loosely) called "the specific heat", but we shall use the correct term: *specific heat capacity*.

Incidentally, we would all find it much easier to understand each other if we all used the word "specific" in contexts such as these to mean "per unit mass".

"Molar" quantities are also intensive quantities. Thus the "molar heat capacity" of a substance is the amount of heat required to raise the temperature of one *mole* of the substance through one degree. I shall have to define "mole" in the next section.

Some authors adopt the convention that extensive quantities are written with capital letters, and the corresponding intensive quantities are written in small letters. Thus C would be the heat capacity of a body in J $\text{C}^{\text{o}\,-1}$ and c would be the specific heat capacity of a substance in J kg^{-1} $\text{C}^{\text{o}\,-1}$. This is undeniably a useful distinction and one that many will find helpful. I have a few difficulties with it. Among these are the following: Some authors (not many) use the opposite convention – small letters for extensive quantities, capitals for intensive. Some authors make exceptions, using P and T for the intensive quantities pressure and temperature. Also, how are we to distinguish between extensive, specific and molar quantities? Three different fonts? This may indeed be a solution – but there is still a problem. For example, we shall become familiar with the equation $dU = T\,dS - P\,dV$. Here U, S and V are internal energy, entropy and volume. Yet the equation (and many others that we could write) is equally valid whether we mean extensive, specific or molar internal energy, entropy and volume. How do we deal with that? Write the equation three times in different fonts?

Because of these difficulties, I am choosing *not* to use the capital letter, small letter, convention, and I am hoping that the context will make it clear in any particular situation. This is, I admit, rather a leap of faith, but let's see how it works out.

1.4: Mole

According to our present state of knowledge, a mass of 12 grams of the ^{12}C isotope of carbon contains 6.022 141 99 × 10^{23} atoms. This number is called Avogadro's number. A mole of an element is the amount of that element that has the same number of atoms as there are atoms in 12 grams of ^{12}C, and a mole of a compound is the amount of that compound that has the same number of molecules as there are atoms in 12 grams of ^{12}C. Likewise a mole of geese is 6.022 141 99 × 10^{23} geese and a mole of baseball caps is 6.022 141 99 × 10^{23} baseball caps.

Why do we define Avogadro's number in terms of 12 grams of carbon-12? This is a long story involving the history of physics and chemistry. None of us was born with a complete knowledge of physics and chemistry and it took a long time to reach our state of knowledge today. We did not always proceed along our path with complete logic, and doubtless, if we did, we might have defined Avogadro's number differently. I am not going to go into the history of how we arrived at this particular definition. Suffice it to say that, if you know that the molecular weight of nitrogen gas (a diatomic molecule) is 28, then 28 grams of nitrogen has Avogadro's number of molecules in it. Indeed the phrase "molecular weight" is not a happy one; it would be better to call it the "molar mass", which is 28 grams.

We might note, however, that when we are doing "SI" calculations, based on MKS units, we shall usually use the kilomole, which is 6.022 141 99 × 10^{26} molecules.

1.5: Prepositions

Prepositions play an important part in thermodynamics! Heat may be supplied **to** a system or lost **from** it. Work may be done **on** a gas or **by** it.

An answer to a question in thermodynamics of “5 joules” is meaningless unless you make it clear and unambiguous whether the system lost 5 joules of heat or gained 5 joules, or whether the gas did 5 joules of work, or you did 5 joules of work on the gas. And it is of no avail to say that the answer is “−5 joules” in the vague hope that I might know what you mean by the minus sign. You must explicitly state in words whether 5 joules was lost or gained – or your reader, or your examiner, will not understand you (and will give you no marks) or will misunderstand you (and will deduct some marks).

I used to tell students that if they wrote “5 joules” without the necessary preposition, they would get no marks for their answer. If they used a preposition, but chose the wrong one (the gas lost 5 joules instead of gaining it) I would take a mark off. Be warned!

1.6: Applicability of Equations

There seem to be lots and lots of equations in thermodynamics. Some of them are of very general applicability. For example the equation $dU = dQ + dW$, which is known as the First Law of Thermodynamics, tells us that the increase in the internal energy of a system is equal to the heat supplied to it plus the work done on it, and it is obviously of very general applicability and is true whatever the nature of the system. An equally well known equation is $PV = RT$. But this equation, which relates pressure, molar volume and temperature, applies *only to an ideal gas*. It doesn't apply to a vapour (which is a gas that is close to the temperature at which it will condense), and still less does it apply to a liquid or a solid. Although we often deal in thermodynamics with a gas held inside a cylinder, thermodynamics is by no means confined to gases, let alone ideal gases.

This section is just an advance warning to be conscious, whenever you see or use an equation, whether the equation is of great generality or whether it applies only to a particular substance or to some special thermodynamic process or to a narrow set of circumstances.

CHAPTER OVERVIEW

2: Partial Derivatives

2.1: Introduction

Any text on thermodynamics is sure to be liberally sprinkled with partial derivatives on almost every page, so it may be helpful here to give a brief summary of some of the more useful formulas involving partial derivatives that we are likely to use in subsequent chapters.

2.2: Partial Derivatives

The equation

$$z = z(x,\ y) \tag{2.2.1}$$

represents a two-dimensional surface in three-dimensional space. The surface intersects the plane y = constant in a plane curve in which *z* is a function of *x*. One can then easily imagine calculating the slope or gradient of this curve in the plane *y* = constant. This slope is $\left(\frac{\partial z}{\partial x}\right)_y$ - the partial derivative of z with respect to x, with y being held constant. For example, if

$$z = y \ln x, \tag{2.2.2}$$

then

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{y}{x}, \tag{2.2.3}$$

y being treated as though it were a constant, which, in the plane *y* = constant, it is. In a similar manner the partial derivative of *z* with respect to *y*, with *x* being held constant, is

$$\left(\frac{\partial z}{\partial y}\right)_x = \ln x \tag{2.2.4}$$

When you have only three variables – as in this example – it is usually obvious which of them is being held constant. Thus ∂*z*/∂*y* can hardly mean anything other than at constant *x*. For that reason, the subscript is often omitted. In thermodynamics, there are often more than three variables, and it is usually (I would say always) essential to indicate by a subscript which quantities are being held constant.

In the matter of pronunciation, various attempts are sometimes made to give a special pronunciation to the symbol ∂. (I have heard “day”, and “dye”.) My own preference is just to say “partial dz by dy”.

Let us suppose that we have evaluated z at *(x , y)*. Now if you increase *x* by δx, what will the resulting increase in *z* be? Obviously, to first order, it is $\frac{\partial x}{\partial x}\delta x$. And if *y* increases by δ*y*, the increase in *z* will be $\frac{\partial z}{\partial y}\delta y$. And if both *x* and *y* increase, the corresponding increase in *z*, to first order, will be

$$\delta z = \frac{\partial z}{\partial x}\delta x + \frac{\partial z}{\partial y}\delta y \tag{2.2.5}$$

No great and difficult mathematical proof is needed to “derive” this; it is just a plain English statement of an obvious truism. The increase in *z* is equal to the rate of increase of *z* with respect to *x* times the increase in *x* plus the rate of increase of *z* with respect to *y* times the increase in *y*.

Likewise if *x* and *y* are increasing with time at rates $\frac{dx}{dt}$ and $\frac{dy}{dt}$, the rate of increase of *z* with respect to time is

$$\frac{dz}{dt} = \frac{\partial z}{\partial x}\frac{dx}{dt} + \frac{\partial z}{\partial y}\frac{dy}{dt}. \tag{2.2.6}$$

2.3: Implicit Differentiation

Equation 2.2.5 can be used to solve the problem of differentiation of an implicit function. Consider, for example, the unlikely equation

$$\ln(xy) = x^2y^3 \tag{2.3.1}$$

Calculate the derivative *dy/dx*. It would be easy if only one could write this in the form *y* = something; but it is difficult (impossible as far as I know) to write *y* *explicitly* as a function of x. Equation 2.3.1 implicitly relates y to x. How are we going to calculate dy/dx?

The curve $f(x, y) = 0$ might be considered as being the intersection of the surface $z = f(x, y)$ with the plane $z = 0$. Seen thus, the derivative dy/dx can be thought of as the limit as δx and δy approach zero of the ratio $\delta y/\delta x$ within the plane $z = 0$; that is, keeping z constant and hence δz equal to zero. Thus equation 2.2.5 gives us that

$$\frac{dy}{dx} = -\left(\frac{\partial f}{\partial x}\right) / \left(\frac{\partial f}{\partial y}\right). \tag{2.3.2}$$

For example, show that, for Rquation 2.3.1,

$$\frac{dy}{dx} = \frac{y(2x^2y^3 - 1)}{x(1 - 3x^2y^3)}. \tag{2.3.3}$$

2.4: Product of Three Partial Derivatives

Suppose x, y and z are related by some equation and that, by suitable algebraic manipulation, we can write any one of the variables explicitly in terms of the other two. That is, we can write

$$x = f(y,\ z), \tag{2.4.1}$$

or

$$y = y(z,\ x), \tag{2.4.2}$$

or

$$z = z(x,\ y). \tag{2.4.3}$$

Then

$$\delta x = \frac{\partial x}{\partial y}\delta y + \frac{\partial x}{\partial z}\delta z, \tag{2.4.4}$$

$$\delta y = \frac{\partial y}{\partial z}\delta z + \frac{\partial y}{\partial x}\delta x \tag{2.4.5}$$

and

$$\delta z = \frac{\partial z}{\partial x}\delta x + \frac{\partial z}{\partial y}\delta y. \tag{2.4.6}$$

Eliminate δy from Equations 2.4.4 and 2.4.5:

$$\delta x\left(1 - \frac{\partial x}{\partial y}\frac{\partial y}{\partial x}\right) = \delta z\left(\frac{\partial x}{\partial z} + \frac{\partial x}{\partial y}\frac{\partial y}{\partial z}\right), \tag{2.4.7}$$

and δz from Equations 2.4.4 and 2.4.6:

$$\delta x\left(1 - \frac{\partial x}{\partial z}\frac{\partial z}{\partial x}\right) = \delta y\left(\frac{\partial x}{\partial y} + \frac{\partial x}{\partial z}\frac{\partial z}{\partial y}\right). \tag{2.4.8}$$

Since z and x can be varied independently, and x and y can be varied independently, the only way in which Equations 2.4.7 and 2.4.8 can always be true is for all of the expressions in parentheses to be zero. Equating the left-hand parentheses to zero shows that

$$\frac{\partial x}{\partial y} = 1/\frac{\partial y}{\partial x} \tag{2.4.9}$$

and

$$\frac{\partial x}{\partial z} = 1/\frac{\partial z}{\partial x}. \tag{2.4.10}$$

These results may seem to be trivial and "obvious" – and so they are, *provided that the same quantity is being kept constant in the derivatives of both sides of each equation*. In thermodynamics we are often dealing with more variables than just x, y and z, and we must be careful to specify which quantities are being held constant. If, for example, we are dealing with several variables, such as u, v, w, x, y, z, it is not in general true that $\frac{\partial u}{\partial y} = 1/\frac{\partial y}{\partial u}$, unless the same variables are being held constant on both sides of the equation.

Return now to Equation 2.4.7. The left hand parenthesis is zero, and this, together with Equation 2.4.10, results in the important relation:

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{2.4.11}$$

2.5: Second Derivatives and Exact Differentials

If $z = z(x, y)$, we can go through the motions of calculating $\frac{\partial z}{\partial x}$ and $\frac{\partial z}{\partial y}$, and we can then further calculate the second derivatives $\frac{\partial^2 z}{\partial x^2}$, $\frac{\partial^2 x}{\partial y^2}$, $\frac{\partial^2 z}{\partial y \partial x}$ and $\frac{\partial^2 z}{\partial y \partial x}$. It will usually be found that the last two, the mixed second derivatives, are equal; that is, it doesn't matter in which order we perform the differentiations.

Example 2.5.1

Let $z = x \sin y$. Show that

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} = \cos y. \tag{2.5.1}$$

Solution

We examine in this section what conditions must be satisfied if the mixed derivatives are to be equal.

Figure II.1 depicts z as a "well-behaved" function of x and y. By "well-behaved" in this context I mean that z is everywhere single-valued (that is, given x and y there is just one value of z), finite and continuous, and that its derivatives are everywhere continuous (that is, no sudden discontinuities in either the function itself or its slope). "Good behaviour" in this sense is the sufficient condition that the mixed second derivatives are equal.

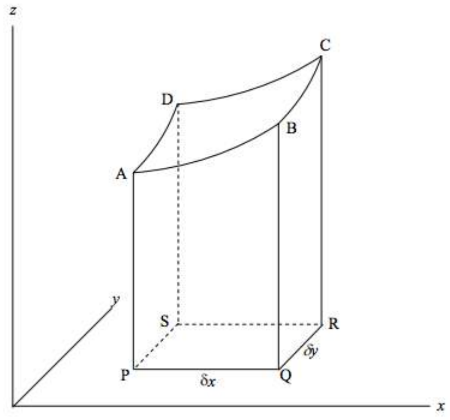


FIGURE II.1

Let us calculate the difference δz in the heights of A and C. We can go from A to C via B or via D, and δz is route-independent. That is, to first order,

$$\delta z = \left(\frac{\partial z}{\partial x}\right)_y^{(A)} \delta x + \left(\frac{\partial z}{\partial y}\right)_x^{(B)} \delta y = \left(\frac{\partial z}{\partial y}\right)_x^{(A)} \delta y + \left(\frac{\partial z}{\partial x}\right)_y^{(D)} \delta x. \tag{2.5.2}$$

Here the superscript (A) means "evaluated at A".

Divide both sides by δx δy:

$$\frac{\left(\frac{\partial z}{\partial y}\right)_x^{(B)} - \left(\frac{\partial z}{\partial y}\right)_x^{(A)}}{\partial x} = \frac{\left(\frac{\partial z}{\partial x}\right)_y^{(D)} - \left(\frac{\partial z}{\partial x}\right)_y^{(A)}}{\partial y}. \tag{2.5.3}$$

If we now go to the limit as δx and δy approach zero (the equation now becomes exact rather than merely "to first order"), this becomes:

$$\frac{\partial^2 z}{\partial x \delta y} = \frac{\partial^2 z}{\partial y \delta x}. \tag{2.5.4}$$

A further property of a function that is well-behaved in the sense described is that if the differential *dz* can be written in the form

$$dz = A(x,\ y)dx + B(x,\ y)dy, \tag{2.5.5}$$

then Equation 2.5.3 implies that,

$$\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}. \tag{2.5.6}$$

A differential *dz* is said to be *exact* if the following conditions are satisfied: The integral of *dz* between two points is route-independent, and the integral around a closed path (i.e. you end up where you started) is zero, and if equations 2.5.3 and 2.5.5 are satisfied.

If a differential such as Equation 2.5.4 is **exact** – i.e., if it is found to satisfy the conditions for exactness – then it should be possible to integrate it and determine *z(x , y)*. Let us look at an example. Suppose that

$$dz = (4x - 3y - 1)dx + (-3x + 2y + 4)dy. \tag{2.5.7}$$

It is readily seen that this is exact. The problem now, therefore, is to find *z(x, y)*.

Let $u = \int (4x - 3y - 1)dx$

So that

$$u = 2x^2 - 3yx - x + g(y). \tag{2.5.8}$$

Note that we are treating y as constant. The "constant" of integration depends on the value of *y* – i.e. it is an arbitrary function of *y*.

Of course *u* is not the same as *z* – unless we can find a particular function *g(y)* such that *u* indeed *is* the same as *z*.

Now $du = \frac{\partial u}{\partial x} + \frac{\partial u}{\partial y} dy$; that is,

$$du = (4x - 3y - 1)dx + \left(-3x + \frac{dg}{dy}\right) dy. \tag{2.5.9}$$

Then *du* = *dz* (and *u* = *z* plus an arbitrary constant) provided that $\frac{dg}{dy} = 2y + 4$. That is,

$$g(y) = y^2 + 4y + \text{constant}. \tag{2.5.10}$$

Thus

$$z = 2x^2 - 3xy + y^2 - x + 4y + \text{constant} \tag{2.5.11}$$

The reader should verify that this satisfies equation 2.5.6. The reader should also try letting

$$\nu = -3xy + y^2 + 4y + f(x) \tag{2.5.12}$$

(where did this come from?) and go through a similar argument to arrive again at equation 2.5.10.

Consider another example

Example 2.5.2

$$dz = 3\ln y\ dx + \frac{x}{y} dy. \tag{2.5.13}$$

You should immediately find that this differential is *not* exact, and, to emphasize that, I shall use the symbol *đz*, the special symbol *đ* indicating an inexact differential. However, given an inexact differential *đz*, it is very often possible to find a function *H(x , y)* such that the differential *dw* = *H(x , y) đz* is exact, and *dw* can then be integrated to find *w* as a function of *x* and *y*. The function *H(x , y)* is called an integrating factor. There may be more than one possible integrating factor; indeed it may be possible to find one simply of the form *F(x)* or maybe *G(y)*. There are several ways for finding an integrating factor. We'll do a simple and straightforward one. Let us try and find an integrating factor for the inexact differential *đz* above. Thus, let *dw* = *F*(*x*)*dz*, so that

$$dw = 3F\ln y\,dx + \frac{xF}{y}dy. \tag{2.5.14}$$

For *dw* to be exact, we must have

$$\frac{\partial}{\partial y}(3F\ln y) = \frac{\partial}{\partial x}\left(\frac{xF}{y}\right). \tag{2.5.15}$$

That is,

$$\frac{3F}{y} = \frac{1}{y}\left(F + x\frac{dF}{dx}\right). \tag{2.5.16}$$

Upon integration and simplification we find that

$$F = x^2, \tag{2.5.17}$$

or any multiple thereof, is an integrating factor, and therefore

$$dw = 3x^2\ln y\,dx + \frac{x^3}{y}dy \tag{2.5.18}$$

is an exact differential. The reader should confirm that this is an exact differential, and from there show that

$$w = x^3\ln y + \text{constant} \tag{2.5.19}$$

To anticipate – what has this to do with thermodynamics? To give an example, the *state* of many simple thermodynamical systems can be specified by giving the values of three *intensive state variables*, *P*, *V* and *T*, the pressure, molar volume and temperature. That is, the state of the system can be represented by a point in *PVT* space. Often, there will be a known relation (known as the *equation of state*) between the variables; for example, if the substance involved is an ideal gas, the variables will be related by *PV* = *RT*, which is the equation of state for an ideal gas; and the point representing the state of the system will then be represented by a point that is constrained to lie on the two-dimensional surface *PV* = *RT* in three-dimensional *PVT* space. In that case it will be necessary to specify only two of the three variables. On the other hand, if the equation of state of a particular substance is unknown, you will have to give the values of all three variables.

Now there are certain quantities that one meets in thermodynamics that are *functions of state*. Two that come to mind are *entropy S* and *internal energy U*. By *function of state* it is meant that *S* and *U* are uniquely determined by the state (i.e. by *P*, *V* and *T*). If you know *P*, *V* and *T*, you can calculate *S* and *U* or any other *function of state*. In that case, the differentials *dS* and *dU* are *exact differentials*.

The internal energy *U* of a system is defined in such a manner that when you add a quantity *dQ* of heat **to** a system and also do an amount of work *dW* **on** the system, the **increase** *dU* in the internal energy of the system is given by

$$dU = dQ + dW. \tag{2.5.20}$$

Here *dU* is an exact differential, but *dQ* and *dW* are clearly not. You can achieve the same increase in internal energy by any combination of heat and work, and the heat you add to the system and the work you do on it are clearly not functions of the state of the system.

Some authors like to use a special symbol, such as *đ*, to denote an **inexact differential** (but beware, I have seen this symbol used to denote an *exact* differential!). I shall not in general do this, because there are many contexts in which the distinction is not important, or, if it is, it is obvious from the context whether a given differential is exact or not. If, however, there is some context in which the distinction is important (and there are many) and in which it may not be obvious which is which, I may, with advance warning, use a special *đ* for an inexact differential, and indeed I have already done so earlier in this section.

2.6: Euler's Theorem for Homogeneous Functions

There is a theorem, usually credited to Euler, concerning homogenous functions that we might be making use of.

A homogenous function of degree *n* of the variables *x*, *y*, *z* is a function in which all terms are of degree *n*. For example, the function $f(x,\ y,\ z) = Ax^3 + By^3 + Cz^3 + Dxy^2 + Exz^2 + Gyx^2 + Hzx^2 + Izy^2 + Jxyz$ is a homogenous function of *x*, *y*, *z*, in which all terms are of degree three.

The reader will find it easy to evaluate the partial derivatives $\frac{\partial f}{\partial x}, \frac{\partial f}{\partial x}, \frac{\partial f}{\partial x}$ and equally easy (if slightly tedious) to evaluate the expression $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z}$. Tedious or not, I do urge the reader to do it. You should find that the answer is $3Ax^3 + 3By^3 + 3Cz^3 + 3Dxy^2 + 3Exz^2 + 3Fyz^2 + 3Gyx^2 + 3Hzx^2 + 3Izy^2 + 3Jxyz.$

In other words, $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = 3f$. If you do the same thing with a homogenous function of degree 2, you will find that $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = 2f$. And if you do it with a homogenous function of degree 1, such as $Ax + By + Cz$, you will find that $x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = f$. In general, for a homogenous function of *x*, *y*, *z*... of degree *n*, it is always the case that

$$x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} + \ldots = nf. \tag{2.6.1}$$

This is Euler's theorem for homogenous functions.

2.7: Undetermined Multipliers

Let ψ(*x, y, z*) be some function of *x, y* and *z*. Then if *x, y* and *z* are independent variables, one would ordinarily understand that, where ψ is a maximum, the derivatives are zero:

$$\frac{\partial\psi}{\partial x}=\frac{\partial\psi}{\partial y}=\frac{\partial\psi}{\partial z}=0. \tag{2.7.1}$$

However, if x, y and z are not completely independent, but are related by some constraining equation such as *f(x, y, z)* = 0, the situation is slightly less simple. (In a thermodynamical context, the three variables may be, for example, three "intensive state variables", *P, V* and *T*, and ψ might be the entropy, which is a function of state. However the intensive state variables may not be completely independent, since they are related by an "equation of state", such as *PV* = *RT*.)

If we move by infinitesimal displacements *dx, dy, dz* from a point where ψ is a maximum, the corresponding changes in ψ and *f* will both be zero, and therefore both of the following equations must be satisfied.

$$d\psi=\frac{\partial\psi}{\partial x}dx+\frac{\partial\psi}{\partial y}dy+\frac{\partial\psi}{\partial z}dz=0, \tag{2.7.2}$$

$$df=\frac{\partial f}{\partial x}dx+\frac{\partial f}{\partial y}dy+\frac{\partial f}{\partial z}dz=0. \tag{2.7.3}$$

Consequently any linear combination of ψ and *f*, such as Φ = ψ + λ*f*, where λ is an arbitrary constant, also satisfies a similar equation. The constant λ is sometimes called an "undetermined multiplier" or a "Lagrangian multiplier", although often some additional information in an actual problem enables the constant to be identified.

In summary, the conditions that ψ is a maximum (or minimum or saddle point), if *x, y* and *z* are related by a functional constraint f (*x, y, z*) = 0, are

$$\frac{\partial\Phi}{\partial x}=0\quad\frac{\partial\Phi}{\partial y}=0,\quad\frac{\partial\Phi}{\partial z}=0, \tag{2.7.4}$$

where

$$\Phi=\psi+\lambda f. \tag{2.7.5}$$

Of course, if ψ is a function of many variables x_1 , x_2 , x_3..., and the variables are subjected to several constraints, such as f = 0, g = 0, h = 0, etc., where *f, g, h*, etc., are functions connecting all or some of the variables, the conditions for ψ to be a maximum (etc.) are

$$\frac{\partial\psi}{\partial x_i}+\lambda\frac{\partial\psi}{\partial x_i}+\mu\frac{\partial\psi}{\partial x_i}+\nu\frac{\partial\psi}{\partial x_i}+\ldots=0,\ i=1,\ 2,\ 3 \tag{2.7.6}$$

2.8: Dee and Delta

We have discussed the special meanings of the symbols ∂ and đ, but we also need to be clear about the meanings of the more familiar differential symbols Δ, δ, and d. It is often convenient to use the symbol Δ to indicate an increment (not necessarily a particularly small increment) in some quantity. We can then use the symbol δ to mean a *small* increment. We can then say that if, for example, $y=x^2$, and if x were to increase by a small amount δx, the corresponding increment in y would be given approximately by

$$\delta y \cong 2x\delta x \tag{2.8.1}$$

That is,

$$\frac{\partial y}{\partial x} \cong 2x. \tag{2.8.2}$$

This doesn’t become exact until we take the limit as \(δ*x*\) and \(δ*y*\) approach zero. We write this limit as $\frac{dy}{dx}$ and then it is *exactly* true that

$$\frac{dy}{dx} = 2x. \tag{2.8.3}$$

There is a valid point of view that would argue that you cannot write dx or dy alone, since both are zero; you can write only the ratio $\frac{dx}{dy}$. It would be wrong, for example, to write

$$dy = 2x\ dx, \tag{2.8.4}$$

or at best it is tantamount to writing 0 = 0. I am not going to contradict that argument, but, at the risk of incurring the wrath of some readers, I am often going to write equations such as Equation 2.8.4, or, more likely, in a thermodynamical context, equations such as

$$dU = TdS - PdV, \tag{2.8.5}$$

even though you may prefer me to say that, for small increments,

$$\delta U \cong T\delta S - P\delta V. \tag{2.8.6}$$

I am going to argue that, in the limit of infinitesimal increments, it is exactly true that $dU = TdS - PdV$. After all, the smaller the increments, the closer it becomes to being true, and, in the limit when the increments are infinitesimally small, it is exactly true, even if it does just mean that zero equals zero. I hope this does not cause too many conceptual problems.

CHAPTER OVERVIEW

3: Temperature

During our studies of heat and thermodynamics, we shall come across a number of simple, easy-tounderstand terms such as *entropy*, *enthalpy*, *Gibbs free energy*, *chemical potential and fugacity*, and we expect to have no difficulty with these. There is, however, one concept that is really quite difficult to grasp, and that is *temperature*. We shall do our best to understand it in this chapter.

3.1: Zeroth Law of Thermodynamics

Perhaps the simplest concept of temperature is to regard it as a potential function whose gradient determines the direction and rate of flow of heat. If heat flows from one body to another, the first is at a higher temperature than the second. If there is no net flow of heat from one body to another, the two bodies are in thermal equilibrium, and their temperatures are equal.

We can go further and assert that

> *If two bodies are separately in thermal equilibrium with a third body, then they are also in thermal equilibrium with each other.*

According to taste, you may regard this as a truism of the utmost triviality or as a fundamental law of the most profound significance. Those who see it as the latter will refer to it as the *Zeroth Law of Thermodynamics* (although the "*zeroth*" does sound a little like an admission that it was added as an afterthought to the other "real" laws of thermodynamics).

We might imagine that the third body is a thermometer of some sort. In fact it need not even be an accurately calibrated thermometer. We insert the thermometer into one of our two bodies (we are not thinking particularly of human bodies here), and it indicates some temperature. Then we insert it into the second body. If it indicates the same temperature as indicated for the first body, then the Zeroth Law asserts that, if we now place our two bodies into contact with each other, there will be no net flow of heat from one to the other. There exists some measure which all three bodies have in common and which dictates that there is no net flow of heat from any one to any other, and the three bodies are in thermal equilibrium. That measure is what we call their **temperature**.

To some, this will sound like saying :"if A and C are at the same temperature, and if B and C are at the same temperature, then A and B are at the same temperature". Others, of philosophical bent, may want to pursue the concept to greater rigor. In any case, at whatever level of rigor is used, what the Zeroth Law establishes is the existence of some quantity called temperature, but it doesn't really tell us how to define a temperature scale quantitatively. It is as if we have established the existence of something called "length" or "mass", but we haven't really specified yet how to measure it or what units to express it in. We could, for example, discuss the concepts of "length" or of "mass" by describing a test to show whether two lengths, or two masses, were *equal*, but without developing any units for expressing such concepts qualitatively. That, I think, is where the Zeroth Law leaves us.

3.2: Temperature Scales I

In everyday practice, we use either the Celsius or the Fahrenheit temperature scales, depending on what we are used to, or the fashion of the day, or what our Government tells us we should be using. In the Fahrenheit scale, the freezing point of water is 32 $^{\mathrm{o}}$F and the boiling point is 212 $^{\mathrm{o}}$F, so that there are 180 F$^{\mathrm{o}}$ between the two fixed points. In the Celsius scale, the freezing point of water is 0 $^{\mathrm{o}}$C and the boiling point is 100 $^{\mathrm{o}}$C, so that there are 100 C$^{\mathrm{o}}$ between the two fixed points. (When Celsius originally introduced his scale, he set the temperature of boiling water as 0, and the temperature of melting ice as 100. That was reversed within a few years!) The Celsius scale was formerly called "the" centigrade scale, but presumably any scale with 100 degrees between two fixed points could be called a centigrade scale, so we now call it (or are supposed to call it) the Celsius scale.

Conversion is obviously by

$$\mathrm{F}=1.8\mathrm{C}+32 \tag{3.2.1}$$

and

$$\mathrm{C}=\frac{\mathrm{F}-32}{1.8}=\frac{5}{9}(\mathrm{F}-32). \tag{3.2.2}$$

Note that "a temperature of so many degrees on the Fahrenheit scale" is written $^{\mathrm{o}}$F and "a temperature of so many degrees on the Celsius scale" is written $^{\mathrm{o}}$C; whereas "a temperature *interval* of so many Fahrenheit degrees" is written F$^{\mathrm{o}}$ and "a temperature interval of so many Celsius degrees" is written C$^{\mathrm{o}}$. In either case, the degrees symbol ($^{\mathrm{o}}$) is mandatory.

In scientific work, we generally use the Kelvin temperature scale. The two fixed points on the Kelvin scale are the absolute zero of temperature, which is assigned the temperature 0 K, and the triple point of the water-ice-steam system, which is assigned the temperature 273.16 K. Thus it could reasonably be said that the Kelvin scale is not a centigrade scale, since it doesn't have 100 degrees between its two fixed points. However, the size of the degree on the Kelvin scale is almost exactly the same as the size of the Celsius degree, because the absolute zero of temperature is about –273.15 $^{\mathrm{o}}$C and the temperature of the triple point is about 0.01 $^{\mathrm{o}}$C. The definition of the Kelvin scale, however, does not mention the Celsius scale, and therefore, although the size of the degrees is about the same on both scales, this is not inherent in the definition. One might speculate about what might happen in the far distant future if people no longer use the Celsius scale and it is totally forgotten. People then will wonder what possessed us to divide the Kelvin scale into 273.16 divisions between its two fixed points!

It would not be good enough to define the upper fixed point of the kelvin scale as the temperature of "melting ice", because this depends on the pressure. The triple point is the temperature at which ice, water and steam are in equilibrium, and it occurs at a temperature of about 0.01 $^{\mathrm{o}}$C and exactly 273.16 K, and a pressure of about 610.6 Pa.

The Kelvin scale starts at zero at the lowest conceivable temperature. The kelvin (K) is therefore regarded as a *unit of temperature*, much as a metre is regarded as a unit of length, or a kilogram as a unit of mass. One therefore does not talk about a temperature of so many "degrees Kelvin", any more than one would talk about a length of so many "degrees metre" or a mass of so many "degrees kilogram". When using the Kelvin scale, therefore, we talk simply of a temperature of "280 kelvins" or "280 K". We do not use the word "degree", nor do we use the symbol $^{\mathrm{o}}$.

In the British Engineering System of units, which is used exclusively in the United States and has never been used in Britain, the Rankine scale is used. The lower fixed point is the absolute zero of temperature, and it is assigned the temperature 0 R, and the size of the rankine is equal to the size of the Fahrenheit degree. Melting ice at 0 ºC has a temperature of 459.67 R, and the triple point has a temperature of 459.688 R.

I doubt whether the Réaumur scale has been used anywhere in the last 50 years, but it has probably been used in the last 100. This had melting ice at 0 o R and steam at 80 $^{\mathrm{o}}$R. I mention this only to point out that if you see a temperature given as so many $^{\mathrm{o}}$R, you might not know whether the Rankine or Réaumur scale is intended! (Strictly, °R would denote degrees Réaumur, while R would denote rankines – but can you trust that?)

In these notes, the Kelvin scale will be the scale that is normally used. There may be occasional use of the Celsius scale, but we shall not use the Fahrenheit, Rankine or Réaumur scales.

3.3: Temperature Scales II

We now know – by definition – the temperatures at the two fixed points on the Celsius and Kelvin scales. But what about temperatures between the fixed points? We could say that the temperature halfway between the melting point of ice and the boiling point of water is 50 ºC, or we could divide the temperature between the two fixed points into 100 equal intervals. But: What do we mean by “halfway” or by “equal intervals” in such a proposal? This leaves us rather stumped.

Here is one suggestion.

We could construct a glass capillary tube with a bulb at the bottom containing mercury, which also extends a short way up the capillary. We could note the length of the mercury column when the tube was immersed in melting ice and call the temperature 0 ºC, and again when it is in boiling water (100 ºC). We could then divide the length of the tube between these two marks into 100 equal intervals of length, and use that to define our temperature scale. But you may ask: How do we know that mercury expands (relative to glass) uniformly with temperature? Well, it expands uniformly, *by definition*, with temperature on the mercury-in-glass temperature scale. Indeed, we can *define* the temperature in the mercury-in-glass scale by

$$t = 100 \times \frac{l_t - l_0}{l_{100} - l_0}\ ^{\circ}\mathrm{C}. \tag{3.3.1}$$

(I am going to use the symbol T in these notes for temperature in *kelvin*. Here I am using t for temperature on the *Celsius* scale.)

If we place the thermometer (for such it is) in a bowl of warm water, and the length of the mercury column is halfway between l_0 and l_{100}, we could say that the temperature of the water in the bowl is, by definition, 50 ºC on the mercury-in-glass scale.

Now let us repeat the experiment with another type of thermometer, using some different property of matter which is also known to vary with temperature. We might choose, for example, to use the electrical resistance R of a length of platinum wire; or the thermoelectric potential difference V that appears when we heat the junction of two different metals; or the pressure P of some gas when it is heated up but kept at constant volume. We could try immersing each of these thermometers into melting ice and boiling water and we could interpolate linearly for intermediate temperatures. Thus, using the resistance of the platinum wire, we could define a platinum resistance temperature scale by

$$t = 100 \times \frac{R_f - R_0}{R_{100} - R_0}\ ^{\circ}\mathrm{C}. \tag{3.3.2}$$

Or we could define a thermoelectric temperature scale by

$$t = 100 \times \frac{V_t - V_0}{V_{100} - V_0}\ ^{\circ}\mathrm{C}. \tag{3.3.3}$$

Or we could define a constant volume gas temperature scale by

$$t = 100 \times \frac{P_t - P_0}{P_{100} - P_0}\ ^{\circ}\mathrm{C}. \tag{3.3.4}$$

But what assurance do we have that all of these temperature scales are the same? What assurance do we have that the resistance of platinum increases linearly on the temperature scale defined by the mercury-in-glass thermometer? What assurance do we have that, when we immerse all of these thermometers in the water that registered 50 ºC for the mercury-in-glass thermometer, they will all register 50 ºC?

The answer is that we have no such assurance.

What we need to do is either choose one particular phenomenon quite arbitrarily to use for our standard temperature scale, or somehow define an *absolute* temperature scale which is absolute in the sense that it is defined independently of the properties of any particular substance. It turns out that it is possible to do the latter, and to define a temperature scale that is absolute and independent of the properties if any particular substance by means of an idealized theoretical concept called a **Carnot Heat Engine**. This imaginary engine uses as its operating medium an equally imaginary substance called an *ideal gas*, and indeed the temperature indicated by a constant volume gas thermometer is identical to the absolute temperature defined by a Carnot engine – provided that the gas used is an ideal gas! The best that can be said for real gases is that, at low pressures, they behave very much like an ideal gas; and indeed if you somehow extrapolate the behaviour or a gas to its behaviour at zero pressure (when there isn’t any gas at all!), it would behave exactly like a real gas.

Until we have discussed what are meant by a real gas and by a Carnot engine, all this has served to do is to underline what we said in the Introduction to this chapter – namely that there are a number of relatively easy concepts in thermodynamics, but temperature is not one of them.

If we do eventually understand what a Carnot engine is and we can construct in our minds a definition of what is meant by an absolute temperature scale, there will remain the problem of reproducing such a scale in practice. That is the purpose of the International Temperature Scale 1990 (ITS90). On this scale a number of fixed points, such as

- the triple point of hydrogen
- the triple point of neon
- the triple point of water
- the freezing point of zinc
- the freezing point of silver
- the freezing point of gold

etc.,

are assigned certain values. In the cases of the six points listed, these values are

- 13.8033
- 24.5561
- 273.16
- 692.677
- 1234.93
- 1337.33

kelvin respectively.

A number of standard instruments are to be used in different temperature ranges, with defined interpolation formulas for temperatures between the fixed points. A complete description of ITS90 would be rather lengthy (see, for example, http://www.omega.com/techref/intltemp.html), but its purpose is to reproduce as precisely as practically possible the absolute temperature scale as defined by the Carnot engine.

CHAPTER OVERVIEW

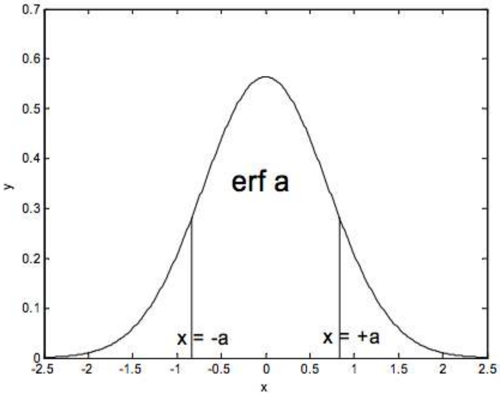
4: Thermal Conduction

4.1: Error Function

Before we start this chapter, let's just make sure that we are familiar with the error function erf a. We may need it during this chapter.

Here is a graph of the gaussian function

$$y=\frac{1}{\sqrt{\pi}}e^{-x^2}. \tag{4.1.1}$$



I have chosen the coefficient $1/\sqrt{\pi}$ so that the area under the curve, from $-\infty$ to $+\infty$ is 1. The maximum value, which occurs at x = 0, is $1/\sqrt{\pi}=0.5642$, and it is easy to show that the half width at half the maximum is $\sqrt{\ln 2}=0.8326$. Also of some interest (though not particularly in this chapter) is the square root of the second moment of area around the y-axis. In a mechanical context this would be called the **radius of gyration**. In a statistical context it would be called the standard deviation. Either way, its value is $1/\sqrt{2}=0.7071$. We shall meet the gaussian function again in Chapter 6.

In the present chapter we shall need to make use of the **error function** erf *a*. This is the area under the gaussian curve from *x* = -*a* to *x* = +*a*:

$$\operatorname{erf} a=\frac{1}{\sqrt{\pi}}\int_{-a}^{+a}e^{-x^2}\,dx. \tag{4.1.2}$$

The area outside the limits x = ±a, which is the area under the two "tails" of the gaussian function, is sometimes called the *complementary error function*:

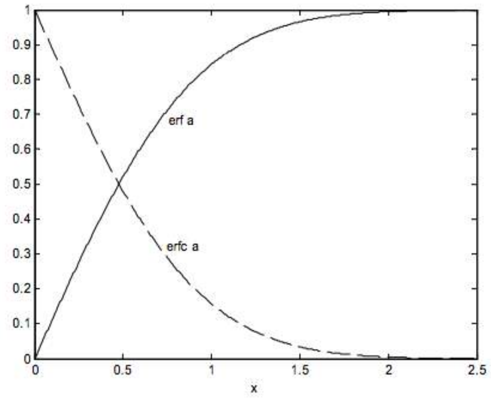
$$\operatorname{erfc} a=1-\operatorname{erf} a \tag{4.1.3}$$

It will be clear that erf a goes from 0 to 1 as a goes from 0 to infinity. Note also that

erfc (one standard deviation) = 0.3173

erfc (two standard deviations) = 0.0455.

Here are graphs of erf *a* (continuous line) and erfc *a* (dashed line) versus *a*.



1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
erf a
erfc a
0
0.5
1
1.5
2
2.5
x

4.2: Introduction

While the subject of thermal conduction is an important one, and obviously a proper topic in the theory of heat, it is not really part of the great logical structure of *thermodynamics*, not does it require a wide or deep knowledge of thermodynamics to understand it, at least at an introductory level. In other words, this chapter is more or less a stand-alone chapter. It is not necessary to understand earlier chapters to understand this one; nor, if your primary interest is in thermodynamics, is it necessary to understand this chapter before proceeding to later ones. That is – if you wish − you can skip this chapter without compromising your understanding of any later ones

4.3: Thermal Conductivity

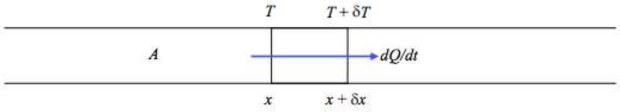


FIGURE IV.1

Figure IV.1 shows heat flowing at a rate *dQ/dt* along a bar of cross-sectional area *A* of material. There is a temperature gradient along the length of the bar (which is why heat is flowing down it). At a distance *x* from the end of the bar the temperature is *T*; at a distance *x* + δ*x* it is *T* + δ*T*. Note that, if heat is flowing in the positive direction as shown, δ*T* must be negative. That is, it is cooler towards the right hand end of the bar. The temperature gradient *dT/dx* is negative. Heat flows in the opposite direction to the temperature gradient.

The ratio of the rate of heat flow per unit area to the negative of the temperature gradient is called the thermal conductivity of the material:

$$\frac{dQ}{dt} = -KA\frac{dT}{dx}. \tag{4.3.1}$$

I am using the symbol K for thermal conductivity. Other symbols often seen are k or λ. Its SI unit is W $\text{m}^{-1}\text{K}^{-1}$.

I have defined it in a one-dimensional situation and for an isotropic medium, in which case the heat flow is opposite to the temperature gradient. One can imagine that, in an anisotropic medium, the rate of heat flow and the temperature gradient may be different parallel to the different crystallographic axes. In that case the heat flow and the temperature gradient may not be strictly antiparallel, and the thermal conductivity is a tensor quantity. Such a situation will not concern us in this chapter.

If, in our one-dimensional example, there is no escape of heat from the sides of the bar, then the rate of flow of heat along the bar must be the same all along the bar, which means that the temperature gradient is uniform along the length of the wire. It may be easier to imagine no heat loss from the sides than to achieve it in practice. If the bar were situated in a vacuum, there would be no loss by conduction or convection, and if the bar were very shiny, there would be little loss by radiation.

Order-of-magnitude values of the thermal conductivities of common substances are

Air	0.03 W $\text{m}^{-1}\text{K}^{-1}$
Water	0.6
Glass	0.8
Fe	80
Al	240
Cu	400

It is easy to imagine how heat may be conducted along a solid, with the vibrations of the atoms at one end of the solid being transmitted to the next atoms by one atom nudging the next, and so on. However, it is evident from the table, and in any case is common knowledge, that some substances (metals) conduct heat much better than others. Indeed, among the metals, there is a close correlation between the thermal and electrical conductivities (at a given temperature). This suggests that the mechanism for thermal conductivity in metals is the same as for electrical conductivity. Heat is conducted in a metal primarily by electrons.

It would be an interesting exercise to find, from the Web or from other references, the thermal and electrical conductivities of a number of metals. It may be found that thermal conductivities, *K*, are sometimes quoted in unfamiliar "practical" units, such as BTU per hour per square foot for a temperature gradient of 1 F° per inch, and converting these to SI units of W $\text{m}^{-1}\text{K}^{-1}$ might be a bit of a challenge. Electrical conductivities, σ, decrease somewhat with rising temperature (so do thermal conductivities, but rather less so), so it would be important to find them all at the same temperature. Then you could see whether the ratio *K*/σ is indeed the same for all metals at a given temperature. This is known as the *Wiedemann-Franz Law*. First-order theory (which we do not give here) predicts that

$$\frac{K}{\sigma T}=\frac{1}{3}\left(\frac{\pi k}{e}\right)^{2}=2.44\times 10^{-8}\mathrm{W}\Omega\mathrm{K}^{-1}. \tag{4.3.2}$$

Here *k* is Boltzmann's constant and *e* is the electronic charge. This prediction is found to be obeyed well at room temperatures and higher, but at low temperatures the electrical conductivity increases rapidly with lowering temperature, and the ratio starts to fall well below the value predicted by equation 4.2.2, approaching zero at 0 K.

The reader may be familiar with the following terms in electricity

Conductivity σ

Conductance *G*

Resistivity ρ

Resistance *R*

They are related by *G* = 1/*R*, σ = 1/ρ, *R* = ρ*l*/*A*, G = σ*A*/*l*,

where *l* and *A* are the length and cross-sectional area of the conductor. The reader probably also knows that resistances add in series and conductances add in parallel. We may define some analagous quantities related to heat flow. Thus resistivity is the reciprocal of conductivity, resistance is *l*/*A* times resistivity, conductance is *A*/*l* times conductivity, and so on. These concepts may come in useful in the following genre of problems beloved of examiners.

A room has walls of area A_1, thickness d_1, thermal conductivity K_1, a door of area A_2, thickness d_2, thermal conductivity K_2, and a window of area A_3, thickness d_3, thermal conductivity K_3, The temperature inside is T_1 and the temperature outside is T_2. What is the rate of heat loss from the room?

We have three conductances in parallel: $\frac{K_1A_1}{d_1}$, $\frac{K_2A_2}{d_2}$,, and $\frac{K_3A_3}{d_3}$, and so we have

$$\frac{dQ}{dt}=\left(\frac{K_1A_1}{d_1}+\frac{K_2A_2}{d_2}+\frac{K_3A_3}{d_3}\right)(T_2-T_1). \tag{4.3.3}$$

Of course, the problem need not be exactly like that. Perhaps you are given the rate of heat loss and asked to find the area of the window. But you get the general idea, and you can probably concoct a few examples yourself. The rate of heat flow is analogous to the current, and the temperature difference is like the EMF of a battery.

4.4: The Heat Conduction Equation

The situation described in Section 4.2 and in figure IV.1 was a *steady-state* situation, in which the temperature was a function of x but not of time. We are now going to consider a more general situation in which the temperature may vary in time as well as in space.

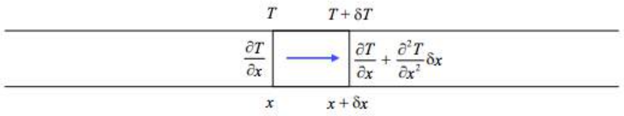


FIGURE IV.3

In this case the temperature gradient is written as a partial derivative, \(\frac{\partial T}{\partial x} and is not uniform down the length of the rod. We'll suppose it is \frac{ \deta T}{\partial x} at *x* and $\frac{\partial T}{\partial x}+\frac{\partial^2 T}{\partial x^2}\delta x$ at x + δx.

Consider the heat flow into and out of the portion between x and x + δx. The rate of flow into this portion at *x* is $-KA\frac{\partial T}{\partial x}$, and the rate of flow out at x + δx is $-KA\left(\frac{\partial T}{\partial x}+\frac{\partial^2 T}{\partial x^2}\delta x\right)$, so that the net flow of heat into that portion is $KA\frac{\partial^2 T}{\partial x^2}\delta x$. This must be equal to $C\rho A\delta x\frac{\partial T}{\partial t}$, where ρ is the density (and hence ρ*A*δ*x* is the mass of the portion), and *C* is the specific heat capacity.

Therefore

$$C\rho\frac{\partial T}{\partial t}=K\frac{\partial^2 T}{\partial x^2}. \tag{4.4.1}$$

This can be written

$$\frac{\partial T}{\partial t}=D\frac{\partial^2 T}{\partial x^2}, \tag{4.4.2}$$

where

$$D=\frac{K}{C\rho} \tag{4.4.3}$$

is the *thermal diffusivity* (m^2 s^{-1}).

Equation 4.3.2 is the *heat conduction equation*. In three dimensions it is easy to show that it becomes

$$T=D\nabla^2 T. \tag{4.4.4}$$

4.5: A Solution of the Heat Conduction Equation

Methods of solving the heat conduction equation are commonly given in courses on partial differential equations. Here we shall look at a simple one-dimensional example.

A long copper bar is initially at a uniform temperature of 0 $^{\text{o}}$C. At time $t = 0$, the left hand end of it is heated to 100 $^{\text{o}}$C. Draw graphs of temperature versus distance x from the hot end of the bar (up to x = 100 cm) at t = 4, 16, 64, 256 and 1024 seconds. Draw also a graph of temperature versus time at x = 5 cm, up to 1024 seconds. Assume no heat is lost from the sides of the bar.

Data for copper:

$K = 400\ \text{W m}^{-1}\ \text{K}^{-1}$

$C = 395\ \text{J kg}^{-1}\ \text{K}^{-1}$

$\rho = 8900\ \text{kg m}^{-3}$

whence

$\text{D} = 1.137 \times 10^{-4}\ \text{m}^2\ \text{s}^{-1}$

The equation to be solved is

$$D\frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} \tag{4.5.1}$$

From the form of this equation, it is obvious (once it has been pointed out!) that a solution could be found in which *T(x, t)* is solely a function of x^2/t, or, for that matter, $x/t^{1/2}$. Thus, let

$$u = x/t^{1/2}, \tag{4.5.2}$$

and you will see that equation 4.4.1 reduces to the second order total differential equation

$$D\frac{d^2T}{du^2} = -\frac{u}{2}\frac{dT}{du}. \tag{4.5.3}$$

Let $T' = dT/du$, and it becomes even easier − a first order equation:

$$D\frac{dT'}{du} = -\frac{1}{2}uT'. \tag{4.5.4}$$

Upon integration, we obtain

$$\ln T' = -\frac{u^2}{4D} + \ln A, \tag{4.5.5}$$

where ln *A* is an integration constant, to be determined by the initial and boundary conditions. (What are the dimensions of *A*?)

That is,

$$T' = A\exp\left[-u^2/(4D)\right]. \tag{4.5.6}$$

We have to integrate again, with respect to *u*:

$$T = A\int \exp\left[-u^2/(4D)\right] du. \tag{4.5.7}$$

Now, $T = 100$ $^{\text{o}}$C at $x = 0$ for any $t > 0$. That is, $T = 100$ for $u = 0$.

And $T = 0$ $^{\text{o}}$C at $t = 0$ for any $x > 0$. That is, $T = 0$ for $u = \infty$.

Therefore

$$100 - 0 = A\int_\infty^0 \exp\left[-u^2/(4D)\right] du. \tag{4.5.8}$$

The integral is slightly difficult though well known. I'll just state the answer here; it is $-\sqrt{\pi D}$. From this, we find that the integration constant is

$$A = -5284\,\mathrm{K\,m^{-1}s^{1/2}}. \tag{4.5.9}$$

We now have

$$100 - T(x,\,t) = A\int_{xt^{-1/2}}^{0} \exp\left[-u^2/(4D)\right] du. \tag{4.5.10}$$

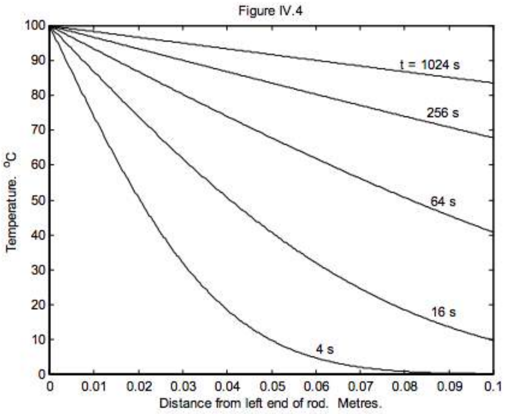
The error function erf(r) is defined by

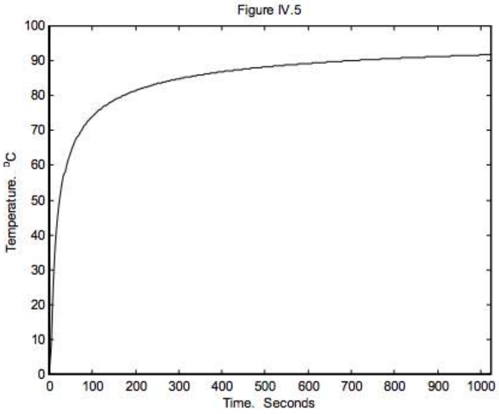
$$\mathrm{erf}(r) = \frac{2}{\sqrt{\pi}}\int_0^r \exp(-s^2) ds, \tag{4.5.11}$$

so that equation 4.4.10 can be written

$$T(x,\,t) = 100 + A\sqrt{\pi D}\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 100\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]. \tag{4.5.12}$$

This function is easy to plot provided that your computer will give you the erf function. The solutions are shown in figures IV.4 and 5.





5: Thermodynamic Processes

We shall be considering what happens when we perform certain *processes* on various *systems*. The processes will usually entail either doing work on a system or adding heat to it, or perhaps we shall allow the system to do work on its surroundings, or the system may lose heat to its surroundings.

Often the system we have in mind will be a gas enclosed by a movable piston inside a cylinder, but it need not be that. The system may be a solid or a liquid, in which there is little change in volume. Or the system may have several phases, such as gas, liquid and solid. There may be several components to the system – for example, a mixture of chemicals. Or the system may be a magnetic material, and we do work on it by putting it in a magnetic field and magnetizing it. Some fundamental thermodynamical laws apply to *any* thermodynamical system and are of great generality. Other laws may apply only to certain specific types of system, and we must always be on our guard to recognize which are general laws applicable to any system, and which are special equations applicable only to particular systems.

We shall, in our imagination, carry out processes under various ideal conditions. Thus, we may imagine a process to be *isothermal* (carried out at constant temperature) or *isobaric* (constant pressure) or *isochoric* (constant volume). We may imagine a process in which no heat is added to or is lost from the system. Such a process is adiabatic.

A process may be *quasistatic* or *nonquasistatic*. Let us imagine that we have a box of gas, and we suddenly heat one wall of the box by pushing that wall up against a source of heat. Not all of the gas will immediately become hotter. At first, the gas near to the heated wall will start to warm up, while the gas at the far end of the box will scarcely be aware of what has happened. Eventually, heat will permeate throughout the box, but this may take some time, and the system is not at all in static equilibrium while these changes are taking place. Likewise, if we have a gas held inside a cylinder by means of a movable piston, and we suddenly move the piston inwards. This will not result in an immediate change to a higher pressure throughout the gas. At the very most the information about the new position of the piston can travel through the gas only at the speed of sound. Considerable local turbulence is likely to be caused, and it will be some time before the gas settles down to its new uniform pressure throughout. Both of these processes are *nonquasistatic*.

For a process to be *quasistatic*, the pressure and temperature of the system must differ from those of its surroundings by only an infinitesimal amount at all times during the process; the process must take place slowly, so that the system passes through an infinite succession of quasi-equilibrium states. The prefix "quasi" is often translated as "almost"; a more precise meaning is "as it were" or "as if it were". The reader will conclude that there cannot ever literally be any process that is truly static. This is also true of other processes, such as isothermal and adiabatic processes. Such processes are limiting theoretical processes. A real process may be intermediate between the ideal extremes, although it may also be quite close to one of the ideal extremes.

CHAPTER OVERVIEW

6: Properties of Gases

Thumbnail: In an ordinary gas, so many molecules move so fast that they collide billions of times every second. (Public Domain; Greg L via Wikipedia)

6.1: The Ideal Gas Equation

In 1660, the Honorable Robert Boyle, Father of Chemistry and seventh son of the Earl of Cork, and one of the founders of the Royal Society of London, conducted certain *Experiments Physico-Mechanical Touching the Spring of the Air*. He held a quantity of air in the closed arm of a J-shaped glass tube by means of a column of mercury and he measured the volume of the air as it was subjected to greater and greater pressures. As a result of these experiments he established what is now known as *Boyle's Law*:

The pressure of a *fixed mass* *of gas held* *at constant temperature* (i.e. in an isothermal process) *is inversely proportional to its volume.*

That is,

$$PV = \text{constant}. \tag{6.1.1}$$

Later experiments showed that the volume of a fixed mass of gas held at constant pressure increases linearly with temperature. In particular, most gases have about the same volume coefficient of expansion. At 0°C this is about 0.00366 $\text{C}^{\text{o}\,-1}$ or 1/273 $\text{C}^{\text{o}\,-1}$.

If you extrapolate the volume of a fixed mass of gas held at constant pressure to lower and lower temperatures, the extrapolated volume would fall to zero at −273 °C. This is not directly the basis of our belief that no temperatures are possible below −273 °C. For one thing, a real gas would liquefy long before that temperature is reached. Nevertheless, for reasons that will be discussed in a much later chapter, we do believe that this is the absolute zero of temperature. In any case:

The volume of a *fixed mass* *of gas held* *at constant pressure* *(i.e. in an isobaric process) is directly proportional to its Kelvin temperature.*

Lastly,

The pressure of a *fixed mass* *of gas held* *at constant volume* *(i.e. in an isochoric process) is directly proportional to its Kelvin temperature.*

If *P*, *V* and *T* are all allowed to vary, these three laws become

$$PV/T = \text{constant} \tag{6.1.2}$$

The value of the constant depends on how much gas there is; in particular, it is proportional to how many moles (hence how many molecules) of gas there are. That is

$$PV/T = RN, \tag{6.1.3}$$

where *N* is the number of moles and *R* is a proportionality constant, which is found to be about the same for most gases.

Of course real gases behave only approximately as described, and only provided experiments are performed over modest ranges of temperature, pressure and volume, and provided the gas is well above the temperature at which it will liquefy. Nevertheless, provided these conditions are satisfied, most gases do conform quite well to equation 6.1.3 with about the same proportionality constant for each.

A gas that obeys the equation

$$PV = NRT \tag{6.1.4}$$

exactly is called an *Ideal Gas*, and equation 6.1.4 is called the *Equation of State for an Ideal Gas*. In this equation, V is the total volume of the gas, N is the number of moles and R is the Universal Gas Constant. The equation can also be written

$$PV = RT. \tag{6.1.5}$$

In this case, V is the *molar volume*. Some authors use different symbols (such as V, v and V_m) for total, specific and molar volume. This is probably a good idea, and it is at some risk that I am not going to do this, and I am going to hope that the context will make it clear which volume I am referring to when I use the simple symbol *V* in any particular situation. Note that, while total volume is an *extensive* quantity, specific and molar volumes are *intensive*.

It is not impossible to go wrong by a factor of 10^3 when using equation 6.1.5. If you are using CGS units, *P* will be expressed in dynes per square cm, *V* is the volume of a mole (i.e. the volume occupied by 6.0221×10^{23} molecules), and the value of the universal gas constant is .8.3145×10^7 erg mole^{-1} K^{-1}. If you are using SI units, P will be expressed in pascal (N m^{-2}), *V* will be the volume of a kilomole (i.e. the volume occupied by 6.0221 x 10^{26} molecules), and the value of the universal gas constant is 8.3145 × 10^3 J kilomole^{-1} K^{-1}. If you wish to express pressure in Torr, atm. or bars, and energy in calories, you're on your own.

You can write equation 6.1.4 (with V = total volume) as $P=\frac{NN_\text{A}}{V}\frac{RT}{N_\text{A}}$ where N_A is Avogadro's number, which is 6.0221 × 10^{23} molecules per mole, or 6.02221 × 10^{26} molecules per kilomole. The first term on the right hand side is the total number of molecules divided by the volume; that is, it is the number of molecules per unit volume, n. In the second term, R/N_A is *Boltzmann's constant*, k = 1.3807 10^{-23} × J K^{-1}. Hence the equation of state for an ideal gas can be written

$$P=nkT. \tag{6.1.6}$$

Divide both sides of equation 6.1.5 by the molar mass ("molecular weight") μ. The density ρ of a sample of gas is equal to the molar mass divided by the molar volume, and hence the equation of state for an ideal gas can also be written

$$P=\frac{\rho RT}{\mu}. \tag{6.1.7}$$

In summary, equations 6.1.4, 6.1.5, 6.1.6 and 6.1.7 are all commonly-seen equivalent forms of the equation of state for an ideal gas.

From this point on I shall use V to mean the *molar volume*, unless stated otherwise, so that I shall use equation 6.1.5 rather than 6.1.4 for the equation of state for an ideal gas. Note that the molar volume (unlike the total volume) is an *intensive* state variable.

In September 2007, the values given for the above-mentioned physical constants on the Website of the National Institute of Science and Technology (http://physics.nist.gov/cuu/index.html) were:

Molar Gas Constant R = 8314.472 (15) J kmole^{-1} K^{-1}.

Avogadro Constant N_A = 6.022 141 79 (30) × 1026 particles kmole^{-1}.

Boltzmann Constant k = 1.380 6504 (24) × 10−23 J K^{-1} per particle.

The number in parentheses is the standard uncertainty in the last two figures.

[There is a proposal, likely to become official in 2015, to give defined exact numerical values to Avogadro's and Boltzmann's constants, namely 6.022 14 x 10^{23} particles mole^{-1} and 1.380 6 x 10^{-23} J K^{-1} per particle. This may at first seem to be somewhat akin to defining π to be exactly 3, but it is not really like that at all. It is all part of a general shift in defining many of the units used in physics in terms of fundamental physical quantities (such as the charge on the electron) rather than in terms of rods or cylinders of platinum held in Paris.]

6.2: Real Gases

How well do real gases conform to the equation of state for an ideal gas? The answer is quite well over a large range of P, V and T, provided that the temperature is well above the critical temperature. We'll have to see shortly what is meant by the critical temperature; for the moment we'll say the ideal gas equation is followed quite well provided that the temperature is well above the temperature at which it can be liquefied merely by compressing it. Air at room temperature obeys the law quite well. Gases in stellar atmospheres also obey the law well, because there is no danger there of the gas liquefying. (In the cores of stars, however, where densities are very large, the gases obey a very different equation of state.)

One measure of how well the law is obeyed by real gases is to measure P, V and T, and see how close $\frac{PV}{RT}$ is to 1. The quantity $\frac{RT}{PV}$ is known as the *compression factor*, and is often given the symbol Z. For most real gases at very high pressures (a few hundred atmospheres), it is found in fact that Z is rather greater than 1. As the pressure is lowered, Z becomes lower, and then, alas, it overshoots and is found to be a little less than 1. Then at yet lower pressures Z rises again. The exact shape of the $Z : P$ curve is different from gas to gas, as is the pressure at which Z is a minimum. Yet, for all gases, *as the pressure approaches zero, PV/T approaches R exactly*. For this reason R is sometimes called the *Universal Gas Constant* as well as the *Ideal Gas Constant*. In the limit of very low pressures, all gases behave very closely to the behaviour of an ideal gas. In Section 6.3 we shall be examining more closely how the compression factor varies with pressure.

Another way to look at how closely real gases obey the ideal gas equation is to plot P versus V for a number of different temperatures. That is, we draw a set of *isotherms*. For an ideal gas, these isotherms, PV = constant, are rectangular hyperbolas. So they are for real gases at high temperatures. At lower temperatures, departures from the ideal gas equation are marked. Typical isotherms are sketched in figure VI.1. Alas, my limited skills with this infernal computer in front of me allow me only to sketch these isotherms crudely by hand.

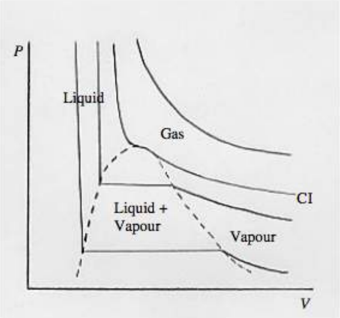


FIGURE VI.1

In the PV plane of figure VI.1, you will see several areas marked "gas", "liquid", "vapour", "liquid + vapour". You can follow the behaviour at a given temperature by starting at the right hand end of each isotherm, and gradually moving to the left – i.e. increase the pressure and decrease the volume. The hottest isotherm is nearly hyperboloidal. Nothing special happens beyond the volume decreasing as the pressure is increased, according to Boyle's law. At slightly lower temperatures, a kink develops in the isotherm, and at the *critical temperature* the kink develops a local horizontal inflection point. The isotherm for the critical temperature is the *critical isotherm*, marked CI on the sketch. Still nothing special happens other than V decreasing as P is increased, though not now according to Boyle's law.

For temperatures below the critical temperature, we refer to the gas as a *vapour*. As you decrease the volume, the pressure gradually increases until you reach the dashed curve. At this point, some of the vapour liquefies, and, as you continue to decrease the volume, more and more of the vapour liquefies, the pressure remaining constant while it does so. That's the horizontal portion of the isotherm. In that region (i.e. outlined by the dashed curve) we have liquid and vapour in equilibrium. Near the right hand end of the horizontal portion, there is just a small amount of liquid; at the left hand end, most of the substance is liquid, with only a small amount of vapour left.

After it is all liquid, further increase of pressure barely decreases the volume, because the liquid is hardly at all compressible. The isotherm is then almost vertical.

The temperature of the critical isotherm is the *critical temperature*. The pressure and molar volume at the horizontal inflection point of the critical isotherm are the *critical pressure* and *critical molar volume*. The horizontal inflection point is the *critical point*.

6.3: Van der Waals and Other Gases

We have seen that real gases resemble an ideal gas only at low pressures and high temperatures. Various attempts have been made to find an equation that adequately represents the relation between *P*, *V* and *T* for a real gas – i.e. to find an *Equation of State* for a real gas. Some of these attempts have been purely empirical attempts to fit a mathematical formula to real data. Others are the result of at least an attempt to describe some physical model that would explain the behaviour of real gases. A sample of some of the simpler equations that have been proposed follows:

van der Waals' equation:

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT. \tag{6.3.1}$$

Berthelot's equation:

$$\left(R+\frac{a}{(TV^2)}\right)(V-b)=RT. \tag{6.3.2}$$

Clausius's equation*:

$$\left(P+\frac{a}{T(V+c)^2}\right)(V-b)=RT. \tag{6.3.3}$$

Dieterici's equation:

$$P(V-b)e^{\frac{a}{(RTV)}}=RT. \tag{6.3.4}$$

Redlich-Kwong:

$$P=\frac{RT}{V-b}-\frac{a}{bT^{\frac{1}{2}}}\left(\frac{1}{V}-\frac{1}{V+b}\right). \tag{6.3.5}$$

Virial equation:

$$PV=A+BP+CP^2+DP^3+\dots \tag{6.3.6}$$

*In Clausius's equation, if we choose $c = 3b$, we get a fairly good agreement between the critical compression factor of a Clausius gas and of many real gases. The meaning of "critical compression factor", and the calculation of its value for a Clausius gas is described a little later in this section.

There are many others, but by far the best known of these is van der Waals' equation, which I shall describe at some length.

It is not possible for the voice-box of an English speaker correctly to pronounce the name van der Waals, although the W is pronounced more like a V than a W, and, to my ear, the v is somewhat intermediate between a v and an f. To hear it correctly pronounced – especially the vowels − you must ask a native Dutch speaker. The frequent spelling "van der Waal's equation" is merely yet another symptom of the modern lamentable ignorance of the use of the apostrophe so much regretted by Lynne Truss.

The units in which the constants *a* and *b* should be expressed sometimes cause difficulty, and they depend on whether the symbol *V* in the equation is intended to mean the specific or molar volume. The following might be helpful.

If V is intended to mean the *specific* volume, van der Waals' equation should be written $\left(P+a/V^2\right)(V-b)=RT/\mu$, where μ is the molar mass ("molecular weight"). In this case the dimensions and SI units of *a* are $\mathrm{M^{-1}\,L^5\,T^{-2}}$ and $\mathrm{Pa\ m^6\ kg^{-2}}$ and the dimensions and SI units of *b* are $\mathrm{M^{-1}\,L^3}$ and $\mathrm{m^3\ kg^{-1}}$

If V is intended to mean the *molar* volume, van der Waals' equation should be written in its familiar form $\left(P+a/V^2\right)(V-b)=RT$. In this case the dimensions and SI units of *a* are $\mathrm{ML^5T^{-2}\ mole^{-2}}$ and $\mathrm{Pa\ m^6\ kmole^{-2}}$ and the dimensions and SI units of *b* are $\mathrm{L^3 mole^{-1}}$ and $\mathrm{m^3\ kmole^{-1}}$

The van der Waals constants, referred to molar volume, of H2O and CO2 are approximately:

H_2O: a = 5.5×10^5 Pa $\mathrm{m^6\ kmole^{-2}}$ · *b* = 3.1×10^{-2} $\mathrm{m^3\ kmole^{-1}}$

CO_2: a = 3.7 × 10^5 Pa m^6 $kmole^{-2}$ b = 4.3 × 10^{-2} m^3 $kmole^{-1}$

The van der Waals equation has its origin in at least some attempt to describe a physical model of a real gas. The properties of an ideal gas can be modelled by supposing that a gas consists of a collection of molecules of zero effective size and no forces between them, and pressure is the result of collisions with the walls of the containing vessel. In the van der Waals model, there are supposed to be attractive forces between the molecules. These are known as van der Waals forces and are now understood to arise because when one molecule approaches another, each induces a dipole moment in the other, and the two induced dipoles then attract each other. This attractive force reduces the pressure at the walls, the reduction being proportional to the number of molecules at the walls that are being attracted by the molecules beneath, and to the number of molecules beneath, which are doing the attracting. Both are inversely proportional to V, so the pressure in the equation of state has to be replaced by the measured pressure P plus a term that is inversely proportional to V^2. Further, the molecules themselves occupy a finite volume. This is tantamount to saying that, at very close range, there are *repulsive* forces (now understood to be Coulomb forces) that are greater than the attractive van der Waals forces. Thus the volume in which the molecules are free to roam has to be reduced in the van der Waals equation. For more on the forces between molecules, see Section 6.8.

However convincing or otherwise you find these arguments, they are at least an attempt to describe some physics, they do represent the behaviour of real gases better that the ideal gas equation, and, if nothing else, they give us an opportunity for a little mathematics practice.

We shall see shortly how it is possible to determine the constants a and b from measurements of the critical parameters. These constants in turn give us some indication of the strength of the van der Waals forces, and of the size of the molecules.

Van der Waals' equation, equation 6.3.1, can be written

$$P=\frac{RT}{V-b}-\frac{a}{V^2}. \tag{6.3.7}$$

A horizontal inflection point occurs where $\frac{\partial P}{\partial V}$ and $\frac{\partial^2 P}{\partial V^2}$ are both zero. That is

$$-\frac{RT}{(V-b)^2}+\frac{2a}{V^3}=0 \tag{6.3.8}$$

and

$$\frac{2TR}{(V-b)^3}-\frac{6a}{V^4}=0. \tag{6.3.9}$$

Eliminate RT/a from these to find the critical molar volume of a van der Waals gas:

$$V_c=3b. \tag{6.3.10}$$

Substitute this into equation 6.3.8 or 6.3.9 (or both, as a check on your algebra) to obtain the critical temperature:

$$T_c=\frac{8a}{27Rb}. \tag{6.3.11}$$

Substitute equations 6.3.10 and 6.3.11 into equation 6.3.7 to obtain the critical pressure:

$$P_c=\frac{a}{27b^2}. \tag{6.3.12}$$

From these, we readily obtain

$$\frac{P_cV_c}{RT_c}=\frac{3}{8}=0.375. \tag{6.3.13}$$

This quantity is often called the critical compression factor or critical compressibility factor, and we shall denote it by the symbol Z_c. For many real gases Z_c is about 0.28; thus the van der Waals equation, while useful in discussing the properties of gases in a qualitative fashion, does not reproduce the observed critical compression factor particularly well.

Let us now substitute $p=P/P_c,\ v=V/V_c,\ t=T/T_c,$ and van der Waals' equation, in which the pressure, volume and temperature are expressed in terms of their critical values, becomes

$$(p+3/v^2)(v-\frac{1}{3})=\frac{8}{3}t. \tag{6.3.14}$$

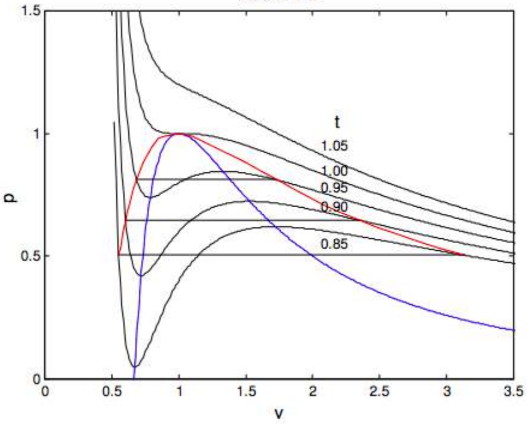
This can also be written

$$3pv^3-(p+8t)v^2+9v-3=0. \tag{6.3.15}$$

For volumes less than a third of the critical volume, this equation does not describe the behaviour of a real gas at all well. Indeed, you can see that $p = \infty$ when $v = 1/3$, which means that you have to exert an infinite pressure to compress a van der Waals gas to a third of its critical volume. You might want to investigate for yourself the behaviour of equations 6.3.14 and 15 for volumes smaller than this. You will find that it goes to infinity at $v = 0$ and 1/3, and it has a maximum between these two volumes. But the equation is of physical interest only for $v > 1/3$, where the variation of pressure, volume and temperature bears at least some similarity to the behaviour of real gases, if by no means exact. In figure VI.2, I show the behaviour of a van der Waals gas for five temperatures – one above the critical temperature, one at the critical temperature, and three below the critical temperature. The locus of maxima and minima is found by eliminating t between equation 6.3.14 and $\partial p/\partial v = 0$. You should try this, and show that the locus of the maxima and minima (which I have shown by a blue line in figure VI.2) is given by

$$p=\frac{3}{v^2}-\frac{2}{v^3} \tag{6.3.16}$$

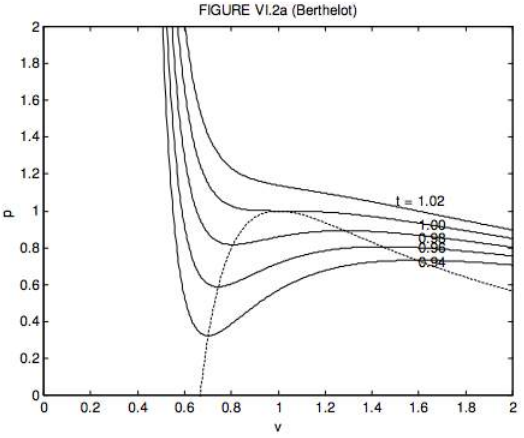
FIGURE VI.2



Don’t confuse the blue curve in this figure (it shows the locus of maxima and minima) with the dashed curve in figure VI.1 (it shows the boundary between phases.). For the temperatures 0.85, 0.90 and 0.95 I have drawn the constant pressure lines where liquid and vapour are in equilibrium in the real fluid. These are drawn so that they divide the van ver Waals curve into two equal areas, above and below. This means that the work done by the real fluid when it changes from liquid to vapour at constant pressure is equal to the work that would be done by its hypothetical van der Waals equivalent along its wiggly path. We shall later see that the placement of the horizontal line is a consequence of the fact that the *Gibbs function* (which we have not yet met) is constant while the liquid and vapour are in equilibrium. The dashed line of figure VI.1 would correspond on figure VI.2 to the locus of the ends of the horizontal lines. I have drawn this locus, which outlines the region where liquid and vapour are in equilibrium, in red in figure VI.2. While the van der Waals equation is only a rough approximation to the behaviour of real gases, it is nevertheless true that, if pressures, temperatures and molar volumes are expressed in terms of the critical pressures, temperatures and molar volumes, the actual equations of state of real gases are very similar. Two gases with the same values of p, v and t are said to be in *corresponding states*, and the observation that the $p : v : t$ relation is approximately the same for all gases is called the *Law of Corresponding States*. We may think of gases as being composed of particles (molecules) and the only difference between different gases is in the sizes of their molecules (i.e. their different van der Waals b constants) and their dipole moments or their electrical polarizabilities (i.e. their different van der Waals a constants). In the dimensionless forms of the equation of state, these van der Waals constants are removed from the equations, and it is not surprising that all gases then conform to the same equation of state.

I leave it to the reader to show that, for a *Berthelot* gas, the critical molar volume, temperature and pressure and the critical compression factor are, respectively, $3b$, $\sqrt{\frac{8a}{27bR}}$, $\frac{1}{b}\sqrt{\frac{aR}{216b}}$ and 0.375, that the equation of state in terms of the dimensionless variables is

$$p=\frac{8t}{3v-1}-\frac{3}{tv^2}, \tag{6.3.17}$$



and that the locus of maxima and minima is

$$p=\frac{1}{v^{1/2}}\left(\frac{4}{v}-\frac{6}{3v-1}\right). \tag{6.3.18}$$

These are shown in figure VI.2a. It will be noted that the critical compression factor is the same as (and hence no better than) for a van der Waals gas.

For a *Clausius* gas, the critical molar volume, temperature and pressure and the critical compression factor are, respectively, $3b+2c$, $\sqrt{\frac{8a}{27(b+c)R}}$, $\frac{1}{(b+c)}\sqrt{\frac{aR}{216(b+c)}}$ and $\frac{3b+2c}{8(b+c)}$.

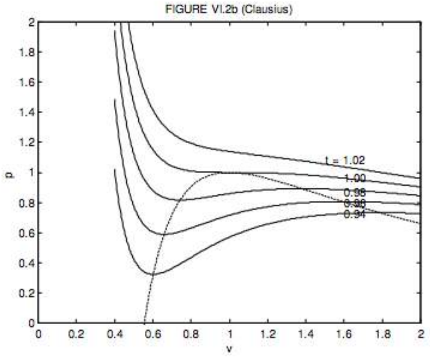
If $c=3b$. these become $3c$, $\sqrt{\frac{2a}{9cR}}$, $\frac{1}{c}\sqrt{\frac{aR}{512c}}$ and $\frac{9}{32}=0.28125$. I choose $c=3b$ because that gives a good agreement with the critical compression factor for many real gases. In dimensionless units, the Clausius equation becomes

$$p=\frac{32t}{9v-1}-\frac{48}{t(3v+1)^2} \tag{6.3.19}$$

The locus of maxima and minima is

$$p=\frac{1}{\sqrt{1+3v}}\left(\frac{80-144v}{1-6v-27v^2}\right)=\frac{16(5-9v)}{(1-9v)(1+3v)^{3/2}} \tag{6.3.20}$$

These are shown in figure VI.2b



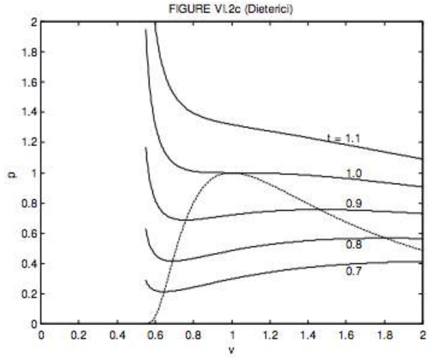
The Clausius equation was hard work. *Dieterici's* is a little easier. The critical molar volume, temperature and pressure and the critical compression factor are, respectively, $2b$, $\frac{a}{4Rb}$, $\frac{a}{4e^2b^2}$ and $2/e^2=0.271$. Note that the critical compression factor is much closer to that of many real gases. The dimensionless form of the Dieterici equation is

$$p=\frac{t}{2v-1}\exp\left(2-\frac{2}{tv}\right). \tag{6.3.21}$$

The locus of maxima and minima is

$$p=\frac{1}{v^2}\exp\left(\frac{2(v-1)}{2v-1}\right). \tag{6.3.22}$$

These are shown in figure VI.2c.



The *Redlich-Kwong* equation of state, like those of van der Waals, Bethelot and Dieterici, has just two parameters (*a* and *b*). All of them are not too bad at temperatures appreciably above the critical temperature, but, close to the critical temperature, the Redlich-Kwong empirical equation agrees a little better than the van der Waals equation does with what is observed for real gases. Obtaining the critical constants in terms of the parameters is done by exactly the same method as for the van der Waals and other equations, but requires perhaps a little more work and patience. The reader might like (or might not like) to try it. For the critical constants I get

$$V_\mathrm{c}=xb, \tag{6.3.23}$$

$$T_\mathrm{c}=y\left(\frac{a}{bR}\right)^{2/3} \tag{6.3.24}$$

and

$$P_c=z\left(\frac{a^2R}{b^5}\right)^{1/3}, \tag{6.3.25}$$

where

$$x=3.847322100 \tag{6.3.26}$$

$$y=0.345039996 \tag{6.3.27}$$

and

$$z=0.029894386. \tag{6.3.28}$$

The critical compression factor is xz/y , which is exactly 1/3. This is not as close to the compression factor of many real gases as the Dieterici critical compression factor is.

We can invert these equations to obtain expressions for *a* and *b* in terms of the critical temperature and pressure (or temperature and volume, or pressure and volume). Thus

$$a=u\left(\frac{R^2T_c^{5/2}}{P_\mathrm{c}}\right) \tag{6.3.29}$$

and

$$b=w\frac{RT_\mathrm{c}}{P_\mathrm{c}}, \tag{6.3.30}$$

where

$$u = 0.427480233 \tag{6.3.31}$$

and

$$w = 0.086640350. \tag{6.3.32}$$

(You can also do this for the other equations of state, of course.)

In order to reproduce these results, you'll have to do a little work to see where all the constants come from. It turns out that the value of the constant x is the positive real root of the equation

$$x^3 - 3x^2 - 3x - 1 = 0. \tag{6.3.33}$$

In the above analysis, I obtained all the constants from a numerical solution of equation 6.3.33, but the solution to this equation (and all subsequent constants) can also be written in surds. Thus, with $f = \sqrt[3]{2} - 1, \quad g = \sqrt[3]{4} - 1, \quad h = \sqrt[3]{16} - 1$, the constants can be calculated from

$$x = \frac{1}{f}, \quad y = g^2, \quad z = \frac{3 - 5g}{g + h}, \quad u = \frac{1}{9f} \text{ and } w = \frac{1}{3} f. \tag{6.3.34}$$

If we now introduce the dimensionless variables $p = P/P_\text{c}, v = VN_\text{c}, t = T/T_\text{c}$, and substitute these and equations 6.3.23-25 into equation 6.3.6, we obtain the dimensionless Redlich-Kwong equation

$$p = \frac{lt}{xv - 1} - \frac{1}{mt^{1/2}} \left(\frac{1}{xv} - \frac{1}{xv + 1} \right), \tag{6.3.35}$$

where

$$l = y/z = 11.54196631 \quad \text{and} \quad m = gz = 0.017559994. \tag{6.3.36}$$

The dimensionless Redlich-Kwong equation is illustrated in figure VI.2d. I have not tried to find an explicit equation for the locus of maxima, but instead I calculated it numerically, illustrated by the dashed line in figure VI.2d.

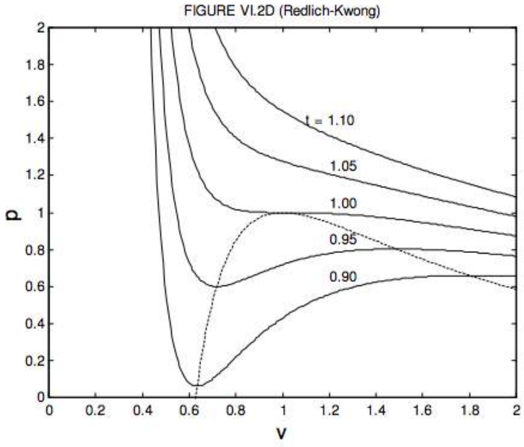


FIGURE VI.2D (Redlich-Kwong)

Here is a summary of the results for the two-parameter equations of state:

$$\begin{array}{lcccccc}
 & P_c & V_c & T_c & Z_c & a & b \\
\text{Van der Waals} & \frac{a}{27b^2} & 3b & \frac{8a}{27Rb} & \frac{3}{8} & \frac{27R^2T_\text{c}^2}{64P_\text{c}} & \frac{RT_\text{c}}{8P_\text{c}} \\
\text{Berthelot} & \frac{1}{b}\sqrt{\frac{aR}{216b}} & 3b & \sqrt{\frac{8a}{27bR}} & \frac{3}{8} & \frac{27R^2T_\text{c}^3}{64P_\text{e}} & \frac{RT_\text{c}}{8P_\text{c}} \\
\text{Dieterici} & \frac{a}{4e^2b^2} & 2b & \frac{a}{4Rb} & 2e^{-2} & \frac{RT_\text{c}}{e^2P_\text{c}} & \frac{4R^2T_\text{c}^2}{e^2P_\text{c}} \\
\text{Redlich-Kwong} & z\left(\frac{a^2R}{b^5}\right)^{1/3} & xb & y\left(\frac{a}{bR}\right)^{2/3} & \frac{1}{3} & u\left(\frac{R^2T_c^{5/2}}{P_c}\right) & w\frac{RT_\text{c}}{P_\text{c}} \\
 & z = 0.0299 & x = 3.85 & y = 0.345 & u = 0.427 & w = 0.0866 &
\end{array} \tag{6.3.37}$$

The reader can try to reproduce these (let me know (jtatum@uvic.ca) if you find any mistakes!) or at least (a useful exercise) verify their dimensions. We mentioned in Section 6.2 that a useful way of indicating how the behaviour of a real gas differs from that of an ideal gas is by plotting the compression factor $Z=\frac{PV}{RT}$ versus pressure. As the pressure approaches zero, the compression factor approaches 1. This is because the molecules are then so far apart that there are no appreciable forces (attractive or repulsive) between them. As the pressure is increased from zero, the compression factor generally at first drops a little below 1, and then rises above 1 as the pressure is increased. It will be interesting to see how the compression factor is expected to vary with pressure for the various "theoretical" gases that we have been discussing. I'll do it just for a van der Waals gas, and I'll use the dimensionless form of van der Waals' equation, which was first given as equation 6.3.14:

$$\left(p+3/v^2\right)\left(v-\frac{1}{3}\right)=\frac{8}{3}t. \tag{6.3.38}$$

The compression factor is $Z=\frac{PV}{RT}$ and the critical compression factor is $Z_c=\frac{P_cV_c}{RT_c}$. From this, we see that $Z=\frac{pv}{t}Z_c$. For a van der Waals gas, $Z_c=\frac{3}{8}$, so that $Z=\frac{3pv}{8t}$. Unfortunately, in order to plot *Z* versus *p* for a given *t*, we have to be able to express *v* in terms of *p*, which means solving equation 6.3.37, which is a cubic equation in $v\left[3pv^3-(p+8t)v^2+9v-3=0\right]$. I have done this numerically, and I show the resulting graphs of *Z* versus p for several temperatures, in figure VI.2e. Notice that at *p* = 1 and *t* = 1, (i.e. at the critical point), the compression factor is 0.375. The *Z* versus *p* curves for real gases have the same general shape, but the precise agreement in numerical detail is not quite so good. Where *Z* > 1, the pressure is greater than that of an ideal gas, the b (repulsive) part of the van der Waals equation being more important than the *a* (attractive) part. Where *Z* < 1, the pressure is less than that of an ideal gas, the *a* (attractive) part of the van der Waals equation being more important than the *b* (repulsive) part. I haven't investigated whether the other "theoretical" equations of state do appreciably better. Why not have a go yourself?!

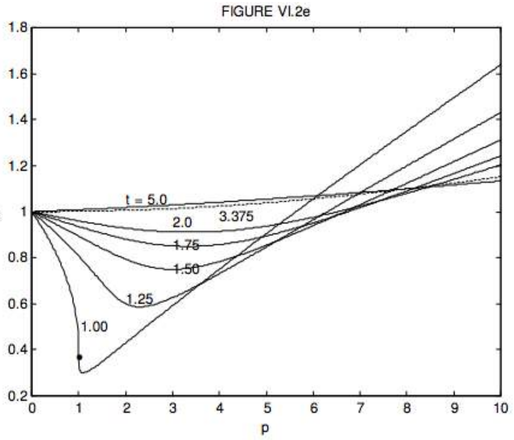


Figure VI.2e. The compression factor Z = PV / RT versus p (pressure in units of the critical pressure for a van der Waals gas, for several values of t (temperature in units of the critical temperature.) For a van der Waals gas the compression factor is greater than 1 for all temperatures greater than *t* = 27/8 = 3.375. At this temperature, the compression factor is close to 1 up to p equals approximately 2, and this temperature is known as the *Boyle temperature*. At the Boyle temperature, the *Z : p* curve is flat and close to 1 for a fairly large range of pressures. Thus, at the Boyle temperature, even a non-ideal gas obeys Boyle's law fairly closely. For a van der Waals gas, the critical temperature is *8a*/(*27Rb*), so the Boyle temperature for a van der Waals is *a*/(*Rb*). The reader should calculate this for H_2O and CO_2, using the values of the van der Waals constants given in this Chapter. The dot on the *t* = 1.00 isotherm at *p* = 1 and *Z* = 0.375 corresponds to the critical point. Anyone who feels in need of more mental exercise might like to ask: For what value of p (other than zero) is *Z* = 1. For example, can you show that, for *t* = 1, *Z* = 1 for *p* = 152/27 = 5.630?

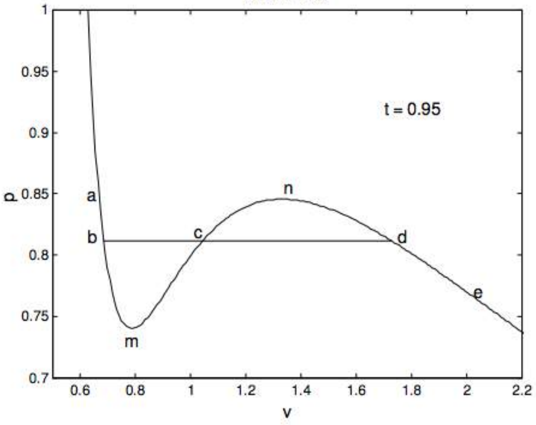
The last proposed empirical equation of state that we mentioned is the virial equation, equation 6.3.6: $PV=A+BP+CP^2+DP^3+\ldots$ This is sometimes written in the form $PV=A+\frac{B}{V}+\frac{C}{V^2}+\frac{D}{V^3}\ldots$, but in these notes we'll use the form of equation 6.3.6. The coefficients *A*, *B*, etc are called the virial coefficients and are functions of temperature. The first coefficient, *A*, is just *RT*. We can also write the virial equation as

$$Z=1+B'P+C'P^2+D'P^3+\ldots \tag{6.3.39}$$

We could measure the coefficient B' for a real gas by plotting Z as a function of pressure in a similar manner to figure VI.2e. The initial slope $\left(\frac{\partial Z}{\partial P}\right)_T$ extrapolated to zero pressure gives the value of B'. At low temperatures B' is negative; at high temperatures B' is positive. At the *Boyle temperature* B' is zero, and at that temperature the compression factor is unity for a large range in pressures, and the gas accordingly closely conforms to Boyle's law. The coefficient C' is small, so the term $C'P^2$ comes into play only at higher pressures. At higher pressures, Z increases, showing that C' is a positive coefficient. The coefficient D' is smaller still than C'

All the mathematically "well-behaved" equations of state below the critical temperature have a maximum and a minimum – i.e. the curve shows a "wiggle". I illustrate this in figure VI.2f. This is the van der Waals isotherm for t = 0.95 in dimensionless variables. It is the same as one of the curves shown in figure VI.2, drawn to a different scale so as to emphasize the "wiggle".

FIGURE VI.2f



Using the little cylinder and piston to the right of the graph, try and imagine what happens to the enclosed liquid or vapour as you move the piston in and out at constant temperature, moving from *a* to *e* and back again on the graph. Start at *e*. The cylinder is filled with vapour. Move the piston inwards, going from *e* to *d*; the pressure increases and the volume decreases. Now a real gas doesn't follow the van der Waals function all the way. At *d*, something different happens. Actually it *is* possible to take a vapour a little way past *d* towards (but not beyond) *n*. That would be a *supercooled vapour*, such as is used in a cloud chamber. It will condense immediately into a line of liquid droplets as soon as a charged particle flies through the vapour. However, what usually happens is that some of the vapour starts to condense as liquid, and we move horizontally from *d* to *b*. As we move the piston down at constant temperature, the volume of course decreases, and more and more liquid condenses in such a manner that the pressure remains constant. In the portion *db*, we have liquid and vapour existing together in the piston, in thermodynamic equilibrium. Near to the *d* end there is only a little liquid; near to the *b* end it is nearly all liquid, with only a little vapour left. Beyond *b*, towards *a*, the space is completely filled with liquid. We can push and push, increasing the pressure greatly, but there is very little change in volume, because the liquid is almost (though not quite) incompressible. The isotherm is very steep there. It is actually possible to take the liquid a little way from *b* towards (but not beyond) *m* without any of it vaporizing. This would be a *superheated liquid*, such as is used in a bubble chamber. It will vaporize immediately into a line of bubbles as soon as a charged particle flies through the liquid.

There will be further important material concerning change of state in Chapters 9 and 14. At present, though, I want to ask: At what pressure does condensation commence? Putting it another way, what is the height of the line bd in figure VI.2f? I have heard it argued that the height of *bd*, (the pressure at which condensation occurs) must be such that the area *bmc* is equal to the area *cnd*. I am not sure that I fully understand the arguments leading to this conclusion. After all, a real gas doesn't conform exactly to a van der Waals equation or any of the other theoretical/empirical equations that we have discussed. But perhaps it is not unreasonable to draw *bd* such that the areas above and below it are equal, and in any case it makes for an interesting (and challenging) computational exercise. The van der Waals equation, in dimensionless variables, is given as equation 6.3.14. Can you calculate the pressure such that the area *bmc* below *bd* is equal to the area *cnd* above it? I make it p = 0.812, which is the height where I have drawn it in the figure. I haven't done the calculation for the other equations. I leave that to you!

6.4: Gas, Vapour, Liquid and Solid

Our description of the behaviour of a real substance in section 6.2 was incomplete in many ways, not least because it made no mention of the solid state. At very low temperatures or at very high pressures, most substances will solidify

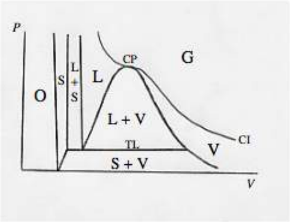


FIGURE V1.3

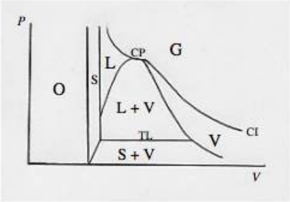


FIGURE V1.4

In figures VI.3 and 4 I have sketched schematically, by hand, the several regions in the *PV*-plane in which a substance exists in its several stages. Unlike in Figure VI.1 and VI.2, I have not drawn *isotherms*. The various lines are intended to represent the boundaries between phases, and are therefore more akin to the dashed curves in figures VI.1 and VI.2. The one exception is the critical isotherm, CI, which is indeed the curve that separates gas from vapour or liquid, but which is also, of course, an isotherm. The difference between figures VI.3 and VI.4 is that figure VI.3 represents a substance that expands when it melts from solid to liquid, while figure VI.4 represents a substance that contracts when it melts from solid to liquid (that is, the solid is less dense than the liquid, and will float upon it.) Most substances expand upon melting, but we have to include those exceptional substances that contract upon melting, because one such substance is one of the most important of all – water.

You can try to understand the figures a little by moving along a horizontal line (isobar) or along a vertical line (isochor) and noticing where phase changes take place. Can you see, for example, where a solid will change to a vapour without going through a liquid phase (sublimation)?

You will note, in the figures, the *critical isotherm* CI, that separates gas from liquid or vapour, and you will note that, at temperatures above the critical temperature, the only phase possible is *gas*, and the substance cannot be liquefied merely by compression. You will note also the *critical point* CP. You will also see the *triple line* TL, along which solid, liquid and vapour co-exist together. What of the region marked O? The substance cannot exist here in solid, liquid or gaseous phase. To that extent, we see that the van der Waals equation may be a little bit better than we thought it was, because you will remember that it went up to infinity at a third of the critical volume. All that this means is that by then the molecules are so tightly jammed together that you simply cannot compress them any further. Although a substance cannot exist in an ordinary solid, liquid or gas phase in the region marked O, if the matter is *degenerate* it will be in this region. The electron structure of the atoms breaks down, so that it then does became possible to jam the atoms closer together. This may mean something to those of you who are familiar with the concept of degenerate matter. If you have not heard of it, do not worry; you are unlikely to come across it unless you visit a white dwarf star, or the core of a massive star, or have to take an examination in astrophysics. For the time being, we shall look the other way and pretend it doesn't exist.

We can get a little more insight by looking at the *PT*-plane. Figure VI.5 shows a substance that expands on melting, and figure VI.6 shows a substance (such as water) that expands on freezing. In the PT-plane, the *triple point* (where solid, liquid and vapour) are in equilibrium with each other, appears as the *triple point*, TP. (In *PVT*-space it is a *line*, although the critical point CP remains a genuine point in *PVT*-space.) The line separating liquid from vapour terminates at the critical point, and the line is often drawn as though it were somehow left hanging in mid-air, so that one is uncertain whether a given point near the critical point represents a gas, a vapour or a liquid. But in the *PT*-plane, the critical isotherm is a vertical line (show as dashed in the figures), and the liquid/vapour boundary terminates at the critical isotherm, and there is no question what phase is represented by a point near to the critical point. To the right of the critical isotherm, we have a gas. To the left, we have either a liquid or a vapour, depending on whether we are above or below the liquid/vapour boundary. As we cross the solid/vapour boundary, below the critical temperature and below the critical pressure (on Mars!) we have a phase change directly from solid to vapour or vapour to solid – i.e. sublimation.

(I have often heard that, below the triple point, a solid will "sublime". I think I prefer the verb "to sublimate".)

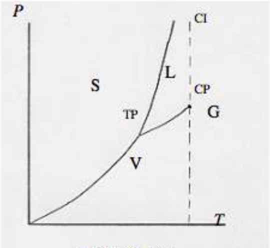


FIGURE VI.5

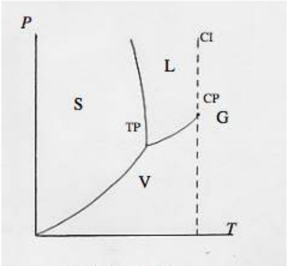


FIGURE VI.6

Really to appreciate these diagrams you need to see and to handle a three-dimensional model in 3- space. My skills at making drawings with my computer are nowhere near good enough yet for me to attempt a three-dimensional drawing, but Mr Charles Card of the University of Victoria was kind enough to photograph for me a model from the University's collection, and I reproduce these below as figures VI 7,8 and 9.

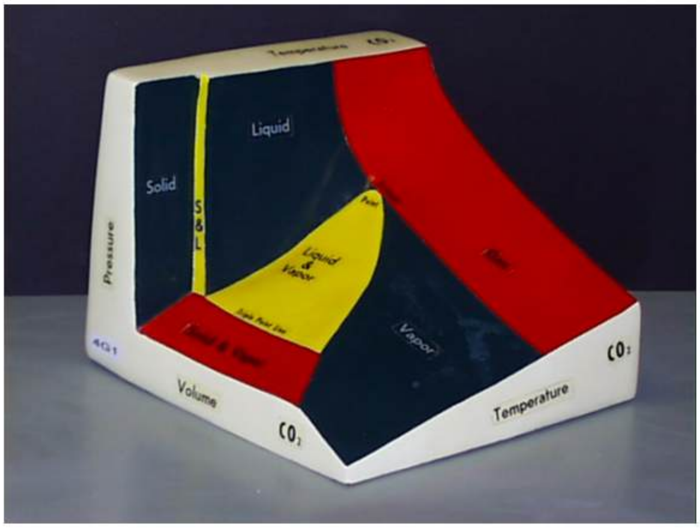


FIGURE VI.7

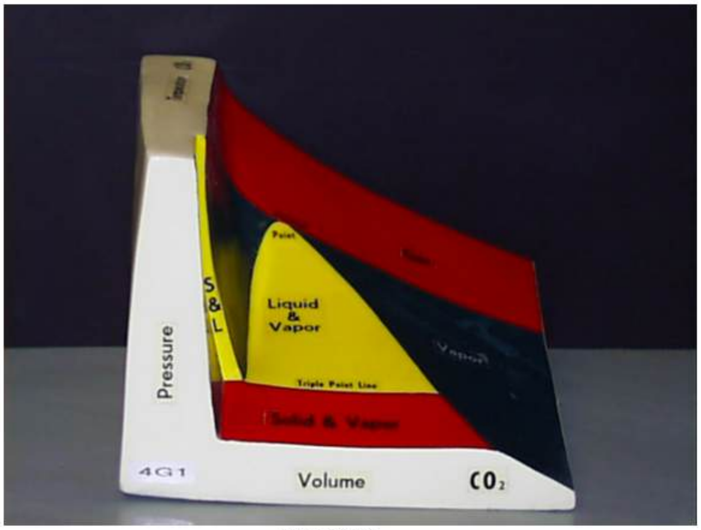


FIGURE VI.8

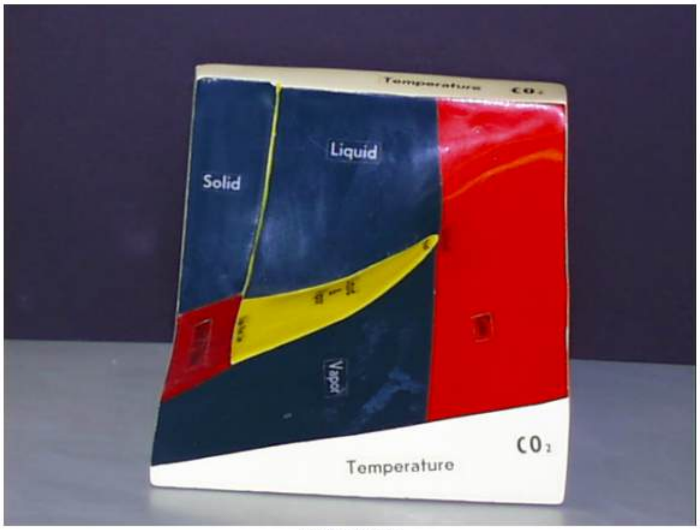


FIGURE VI.9

I now give some numerical values for the critical temperature and pressure, the compression factor, and the temperature and pressure of the triple point for H_2O and for CO_2. These are not intended as definitive values. I looked them up in a number of sources and I found a surprisingly wide range of the numbers quoted. They are given here merely to give the reader a rough idea of what the values are for these two substances. The temperature quoted for the triple point of H_2O is, of course, exact, being one of the fixed points of the Kelvin scale. Recall that one atmospheric pressure is about 1.01×10^5 Pa.

The reader might like to see whether these numbers are compatible with the numbers I gave for the van der Waals constants in Section 6.3. Exact agreement is not to be expected, because the figures I quote are only approximate and are gleaned from a variety of sources and also, of course, neither gas can be expected to obey van der Waals' equation exactly. If the numbers seem to be wildly discrepant, please let me know.

We who live on the surface of Earth are familiar with water in its solid, liquid and vapour forms, and this might suggest that the conditions on the surface of Earth, the temperature and pressure, must be close to the triple point of water. We see from the above table that the triple point of water (which is defined to be 273.16 K = 0.01 ºC in the International Temperature Scale), is indeed near our typical ambient temperatures, but the triple point pressure of water is 611.73 Pa, which is only about 0.006 atm. However, we are near the triple point if the *partial pressure* of water vapour in the atmosphere is close to 0.006 atm, which it often is. So we are indeed close to the triple point, which is why we so often see water in its three phases. Incidentally, the $P : T$ diagram for the water system is a good deal more complicated that the ideal diagram of figure VI.6, particularly in the "solid" region, since there are apparently many (about 15) different forms, or phases, of water ice.

Some idle thoughts on vapours. There is a question of how to spell "vapour". In the United States, "vapor" is usual, and in the United Kingdom "vapour" is usual. "Vaporize" is a bit trickier. The spelling "vaporize" is usual in the United States, but what to do in the United Kingdom? Is it vapourize, vapourise, vaporize or vaporise? Is there a u or no u? Is it z or s? To answer the first question: In the United Kingdom, the u, as in the United States, is omitted. Only weak spellers and those who would try to be "more English than the English" would try to insert a u. As for s or z, either seems to be used in the United Kingdom. Etymologically, z would be the better choice, so the spelling "vaporize" is perfectly acceptable on both sides of the Atlantic Ocean.

More idle thoughts on vapours. Is a "vapour" a "gas? What is a "fluid"? And is glass a liquid? Some authors treat "gas" and "vapour" as though they were quite different things: a gas is not a vapour, and a vapour is not a gas. Others regard a "vapour" as being a sort of gas – namely a gas whose temperature is below the critical temperature and which can be liquefied by increasing the pressure. In that case, what do you call a gas that is above the critical temperature? The term permanent gas is often used. Thus a vapour is a gas below its critical temperature, and a permanent gas is a gas above its critical temperature.

A *fluid* is something that flows. Thus liquids and gases (including vapours) are fluids. There is, you would imagine, always a clear distinction between a liquid and a gas. But is the distinction always so clear? I admit that I have never actually seen the phenomenon that I am about to describe, but it is described so often that I presume someone has seen it! Consider a closed container with a liquid in equilibrium with its vapour. The liquid and vapour are separated by a sharp, horizontal boundary. That is to say, the system is on the line separating liquid and vapour in figures VI.5 and 6. This line can be regarded, if you like, as a graph of boiling point versus temperature, or equally of vapour pressure versus temperature. If you raise the pressure, the boiling point increases; or if you increase the temperature, the vapour pressure increases. More liquid will enter the vapour state, and, as the pressure of the vapour increases, so does its density. The liquid, on the other hand, is almost incompressible, and, because of thermal expansion, its density decreases. As we move up the line separating liquid form vapour in the $P:T$ plane, the density of the vapour increases and the density of the liquid decreases. Their densities become more and more equal until, as we approach the critical point, the boundary between liquid and vapour becomes less and less distinct, and less constrained by gravity to be horizontal, until eventually, at the critical point, the distinction between liquid and vapour blurs and ultimately disappears. So – what have you got then? It is certainly a *fluid*, but are you going to call it a gas, a vapour or a liquid? Since none of these words would seem to have a stronger claim than either of the others, some authors refer to the substance when a little above and to the right of the critical point in the $P:T$ plane as a *supercritical fluid.*

There is also the question as to whether glass is a solid or a liquid. A famous radio personality many years ago, on a “Brains Trust” programme broadcast by the British Broadcasting Corporation, Professor C. E. M. Joad, was famous for his sentence: “It all depends on what you mean by…” So I suppose the question as to whether glass is a liquid or a solid depends on what you mean by a liquid or a solid. The moment when I drop a tumbler and it shatters into many viciously sharp fragments is not a good moment to convince me that glass is a liquid. Those who assert that glass is a liquid say that it has not got a solid crystalline structure, and that it *flows*, albeit very slowly. It has a very large viscosity. We are told that windows in ancient mediaeval cathedrals are thicker at the bottom than at the top, as a result of the viscous liquid flow over the centuries. I don’t know if any of the many people who have told me that have actually personally measured the thickness of a cathedral window.

At any rate, before you started this chapter, you had a very clear idea in your mind about the differences between a solid, liquid and a gas. Now that I have painstakingly explained it all, you are completely confused, and are no longer at all sure that you know the difference.

6.5: Kinetic Theory of Gases- Pressure

There will be more about *macroscopic PVT* relations for gases when we go further into thermodynamics. In this section, we deal with *microscopic* properties, and how pressure and temperature are related to the number density of molecules and their speed.

We shall consider an ideal gas, containing *n* molecules per unit volume, each of mass m, held in a cubical box of side *l*. The velocity of a particular molecule is to be denoted by **c** = *u***i** + *v***j** + *w***k**. Here *u*, *v*, *w* are the components of the velocity parallel to the sides of the box. As ever, I shall use the word *velocity* to mean "velocity" and the word *speed* to mean "speed". Thus the velocity of the molecule is **c** and its speed is *c*. We are going to start by calculating the pressure on the walls, assumed to be caused by the collisions of millions of molecules repeatedly colliding with the walls.

("Why do you keep banging your head against the wall?" "Because it feels so good when I stop.")

Consider the *x*-motion. Assuming that collisions are elastic, we note that the change of the *x*-component of momentum when a molecule bounces off a *yz*-wall is 2*mu*. The time taken to cross to the other side of the cube and back again is 2*l*/*u*. The number of collisions that this molecule makes with one *yz*-wall per unit time is *u*/(2*l*). The rate of change of momentum of that molecule at that wall is therefore 2*mu* x *u*/(2*l*) = mu^2/l. The rate of change of the *x*-component of the momentum at that wall of all the nl^3 molecules in the box is $nl^3 \times m\overline{u^2}/l = nml^2\overline{u^2}$. That is, the force on that wall is $nml^2\overline{u^2}$, and so the pressure on the wall is $nm\overline{u^2}$. But $\overline{u^2} = \overline{v^2} = \overline{w^2}$ (that’s assuming that the velocities are isotropic and there’s no wind) and $\overline{u^2} + \overline{v^2} + \overline{w^2} = \overline{c^2}$ (that’s Pythagoras’s theorem), and therefore $\overline{u^2} = \frac{1}{3}\overline{c^2}$. So the pressure is

$$P = \frac{1}{3}nm\overline{c^2} = \frac{1}{3}\rho\overline{c^2}. \tag{6.5.1}$$

Here ρ is the density = mass ÷ volume = molar mass ÷ molar volume = μ/V, (here V = molar volume) and therefore

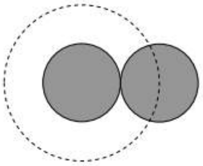
$$PV = \frac{1}{3}\mu\overline{c^2}. \tag{6.5.2}$$

But $\frac{1}{3}\mu\overline{c^2}$ is $\frac{2}{3}$ of the translational kinetic energy of a mole of gas, and we already know that *PV* = *RT*, so that we deduce that the *translational kinetic energy of the molecules in a <u>mole</u> of gas* is equal to $\frac{3}{2}RT$. That is to say the <u>mean</u> translational kinetic energy per <u>molecule</u> is $\frac{3}{2}kT$, where *k* is Boltzmann's constant (see Section 6.1).

6.6: Collisions

In this section, we are going to ask: What is the mean time between intermolecular collisions? What is the mean free path between collisions? How many intermolecular collisions are there per unit volume per unit time? How many collisions with the walls of a containing vessel are there per unit area per unit time? Since I know little chemistry, I shall assume that molecules are hard spheres of diameter d. This may not be too bad for monatomic gases such as the rare gases. For others, the assumption is tantamount to assuming that molecules repel each other when their centres of mass approach within a distance d. In any case, we shall assume that the *collision cross-section* is of area πd^2.

Notice, from the sketch below, that two equal spheres collide when their centres are separated by their *diameter* d, and consequently the collision cross section (shown as a dashed circle) is of area πd^2.



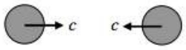
In fact in what follows, I'm just going to call the area of the collision cross section σ; in doing that, I don't even have to assume that its shape is circular.

In time t, a molecule moving with speed c sweeps out a cylinder of volume σct. If there are n molecules per unit volume, the number of collisions that that particular molecule will experience in time t would appear to be σctn, which is to say that the number of collisions it experiences in unit time is σcn. Thus the mean time τ between collisions would appear to be), $\tau = 1/(\sigma cn)$ and the mean free path λ between collisions is). $\lambda = 1/(\sigma n)$.

But this isn't quite right, because we have not taken into account the fact that all the molecules in the above-mentioned cylinder are moving. It is not as though our hero molecule were colliding with a set of stationary molecules. The relevant speed to use in this analysis is the *mean relative speed* between molecules, and this is a little greater than the speed c of each. Let's see if we can do a little better.

Let's start by supposing that all of the molecules are moving with speed c. There are two extreme sorts of collision:

The "head on" collision:



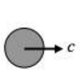
For such a collision, the relative speed between the molecules is $2c$.

Then there is the sort of collision in which one molecule barely catches up with another one:

In that case the relative speed is zero.

The average relative speed is evidently somewhere between 0 and $2c$.

These are extreme cases. The "average" situation is somewhat in between. We may argue that the "average" situation is for the two molecules to be travelling in perpendicular paths:



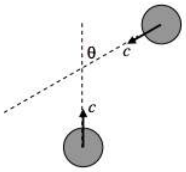
If we think of this as the "average" situation, then we may argue that the "average" relative speed between two molecules is $\sqrt{2}c$. In that case, we may conclude that the mean time between collisions is $\tau = 1/(\sqrt{2}\sigma cn)$, and the mean free path is

$\lambda = 1/(\sqrt{2}\sigma n)$.

This argument may or may not be completely convincing, but it is probably closer to the mark than our previous effort.

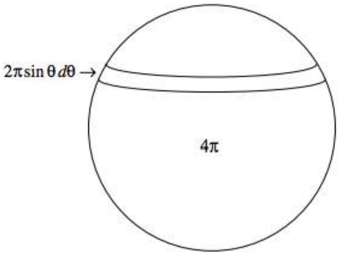
Let's see if we can make a further improvement. As before, we'll suppose that each molecule is moving with speed *c*.

Suppose our hero molecule to be moving upward with speed c, and another molecule approaches at an angle θ, as in the sketch below.



By vector addition of velocities, it will be seen (a little thought will be needed) that the relative speed of approach between the two molecules is $\sqrt{2}c(1+\cos\theta)^{1/2}$.

Now the fraction of molecules approaching from angles between θ and θ + *d*θ is $\frac{1}{2}\sin\theta d\theta$. This is because the area of an elemental zone of a sphere of unit radius between θ and θ + dθ is 2πsinθ*d*θ, and the total area of the sphere is 4π - see the sketch below:



Thus the mean relative speed of all the molecules is $\int_0^\pi \sqrt{2}c(1+\cos\theta)^{1/2} \times \frac{1}{2}\sin\theta d\theta$, which works out to be $\frac{4}{3}c$.

In this model, then, the mean time between collisions would be $\tau = \frac{1}{\frac{4}{3}\sigma cn}$, and the mean free path would be $\lambda = \frac{1}{\frac{4}{3}\sigma n}$.

However, we have still assumed that all the molecules are moving at the same speed. I am told (but I have not verified it myself) that, if you take account of the Maxwell-Boltzmann distribution of speeds (see Section 6.7), the mean relative speed of collision is $\sqrt{2}\bar{c}$, where $\bar{c}$ is the mean speed of the Maxwell-Boltzmann distribution (equal to $\sqrt{\frac{8kT}{\pi m}}$.) If that is so, then we obtain $\tau = \frac{1}{\sqrt{2}\sigma\bar{c}n}$ and $\lambda = \frac{1}{\sqrt{2}\sigma n}$.

In any case, since molecules are not hard spheres (they are neither spheres nor hard) and the details of a "collision" depend on the shape of the molecules and the force law between them, it may not be meaningful to try to obtain an extremely precise formula for the mean free path, but instead settle for $\tau = \frac{1}{b\sigma\bar{c}n}$ and $\lambda = \frac{1}{b\sigma n}$, and if you wish to take $b \approx \sqrt{2}$, you won't be far out.

Of more interest would be to calculate the mean time between collisions for various pressures and temperatures, and ask how does this compare, for example, with the mean lifetime of an atom in an excited atomic level, or a metastable level. Or to compare the mean free path between collisions with the mean nearest-neighbour distance between molecules in a gas. I think under typical familiar conditions, you'll find that the mean free path is rather longer than the mean nearest-neighbour distance.

Also of interest is the number of collisions per unit volume per unit time. If we suppose that a single molecule experiences $b\sigma\bar{c}n$ collisions per unit time, and there are *n* molecules per unit volume, then the number of collisions per unit volume per unit time is

$$Z = \frac{1}{2}b\sigma\bar{c}n^2.$$

The factor of $\frac{1}{2}$ is necessary so that we don't count collisions of A with B and of B with A as two different collisions.

Another useful result is that the number of molecules striking the walls of a containing vessel per unit area per unit time is

$$\frac{1}{4}n\bar{c}$$

To avoid repetition, I don't derive this here, but you will find a derivation in Chapter 1 Section 1.17 of Stellar Atmospheres, where I do the derivation with photons rather than with molecules. The only difference is that, in the case of the photons, all are moving at the same speed c (the speed of light), whereas here we have a distribution of speeds, and we use $\bar{c}$, the mean speed of the molecules.

6.7: Distribution of Speeds

I am tempted to start by saying "Let $f(u)du$ be the fraction of molecules of which the x-component of their velocities is between u and $u + du$." But we can go a little further than this with the realization that this distribution must be symmetric about $u = 0$, and therefore, whatever the function is, it must contain only even powers of u. So we can start with:

Let $f(u^2)du$ be the fraction of molecules of which the x-component of their velocities is between u and $u + du$. Then, unless there is a systematic flow on the x-direction or the x-direction is somehow special, the fraction of molecules with y velocity components between v and $v + dv$ is $f(v^2)dv$, and the fraction of molecules with z velocity components between w and $w + dw$ is $f(w^2)dw$. The fraction of molecules in a box $du\ dv\ dw$ of velocity space is $f(u^2)f(v^2)f(w^2)du\ dv\ dw$. Since the distribution of velocity components is independent of direction, this product must be of the form

$$f\left(u^2\right) f\left(v^2\right) f\left(w^2\right)=F\left(c^2\right) \tag{6.7.1}$$

or

$$f\left(u^2\right) f\left(v^2\right) f\left(w^2\right)=F\left(u^2+v^2+w^2\right) \tag{6.7.2}$$

(Question: Dimensions of f? Of F?)

It is easy to see that this is satisfied by

$$f\left(u^2\right)=A e^{\pm u^2 / c_n^2}, \tag{6.7.3}$$

where A and c_m are constants to be determined. It should also be clear that, of the two possible solutions represented by equation 6.7.3, we must choose the one with the minus sign.

Since we must have

$$\int_{-\infty}^{\infty} f\left(u^2\right) d u=1 \tag{6.7.4}$$

it follows that

$$A=\frac{1}{c_\mathrm{m} \sqrt{\pi}}. \tag{6.7.5}$$

(To see this, you have to know that $\int_0^{\infty} e^{-a x^2} d x=\frac{1}{2} \sqrt{\frac{\pi}{a}}$.)

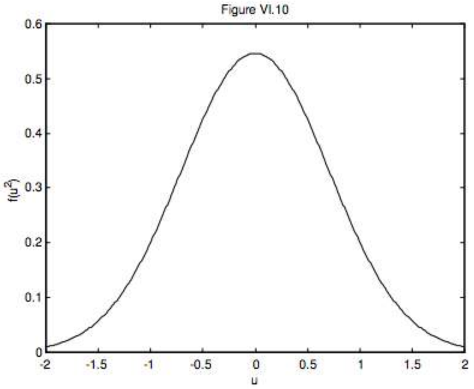
Thus we now have

$$f\left(u^2\right)=\frac{1}{c_\mathrm{m} \sqrt{\pi}} e^{-u^2 / c_m^2} \tag{6.7.6}$$

This is the *gaussian* distribution of a velocity component. We shall shortly find a physical interpretation for the constant c_m.

The area under the curve represented by equation 6.7.9 is, of course, unity; the maximum value of (is) /(1). 2 f u cm π

Figure VI.10 illustrates this distribution. In this figure, the unit of speed is c_m. The area under the curve is 1. The maximum (at u = 0) is $1/\sqrt{\pi}=0.564$. *Exercise*: Show that the FWHM (full width at half maximum) is $2\sqrt{\ln 2}c_\mathrm{m}=1.665c_\mathrm{m}$. This gives one physical interpretation of c_m; we shall soon give another one, which will explain the use of m as a subscript.

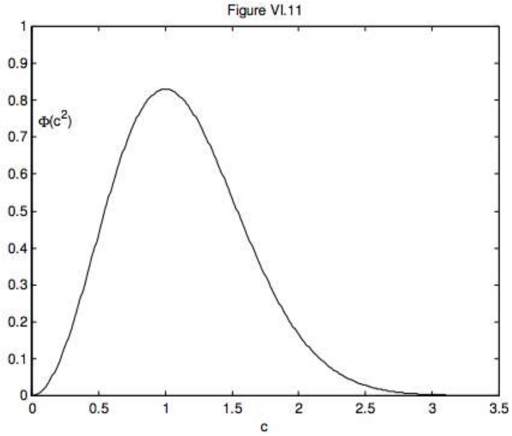


The gaussian distribution deals with *velocity components*. We deal now with *speeds*. The fraction of molecules having speeds between c and $c + dc$ is $F(c^2)$ times the volume of a spherical shell in velocity space of radii c and $c + dc$. (Some readers may recall a similar argument in the Schrödinger equation for the hydrogen atom, in which the probability of the electron's being at a distance between r and $r + dr$ is the probability density ψψ* times the volume of a spherical shell.

You'll notice that physics becomes easier and easier, because you have seen it all before in different contexts. In the present context, F is akin to the ψψ* of wave mechanics, and it could be considered to be a "speed density".) Thus the fraction of molecules having speeds between c and $c + dc$ is

$$\Phi\left(c^2\right) dc = \frac{4c^2}{c_m^3\sqrt{\pi}} e^{-c^2/c_m^2} dc \tag{6.7.7}$$

I shall leave it to those who are skilled at calculus to show that $\int_0^\infty \Phi\left(c^2\right) dc = 1$, and also to show that the maximum of this distribution occurs for a speed of $c = c_\text{m}$ and that the maximum value of $\Phi\,(c^2)$ is $4/\left(c_\text{m}e\sqrt{\pi}\right)$. This provides another interpretation of the constant c_m. The speed at which the maximum of the distribution occurs is called the mode of the distribution, or the *modal speed* – hence the subscript m. Equation 6.7.10 is the *Maxwell-Boltzmann* distribution of speeds. It is shown in figure VI.7, in which the unit of speed is c_m. The area is 1, and the maximum is $4/(e\sqrt{\pi}) = 0.830$.



The *mean* speed $\bar{c}$ is found from $\int_0^\infty c\Phi\left(c^2\right) dc$ and the *root mean square* speed c_RMS is found from $c_\text{RMS}^2 = \int_0^\infty c^2\Phi\left(c^2\right) dc$. If you have not encountered integrals of this type before, you may find that the first of them is easier than the second. If you can do these integrals, you will find that

$$\bar{c} = \frac{2}{\sqrt{\pi}} c_\text{m} \text{ and } c_\text{RMS} = \sqrt{\frac{3}{2}} c_\text{m} \tag{6.7.8}$$

The root mean square (RMS) speed, for which I am here using the symbol c_RMS, is of course the square root of $\overline{c^2}$. We have seen from Section 6.5 that the mean kinetic energy per molecule, $\frac{1}{2}m\overline{c^2}$, is equal to $\frac{3}{2}kT$, so now let's bring it all together:

$$c_{\mathrm{m}}=\frac{\sqrt{\pi}}{2}\bar{c}=0.886\bar{c}=\sqrt{\frac{2}{3}}c_{\mathrm{RMS}}=0.816c_{\mathrm{RMS}}=\sqrt{\frac{2kT}{m}}=1.414\sqrt{\frac{kT}{m}} \tag{6.7.9}$$

$$\bar{c}=\frac{2}{\sqrt{\pi}}c_{\mathrm{m}}=1.128c_{\mathrm{m}}=\sqrt{\frac{8}{3\pi}}c_{\mathrm{RMS}}=0.921c_{\mathrm{RMS}}=\sqrt{\frac{8kT}{\pi m}}=1.596\sqrt{\frac{kT}{m}} \tag{6.7.10}$$

$$c_{\mathrm{RMS}}=\sqrt{\frac{3}{2}}c_{\mathrm{m}}=1.225c_{\mathrm{m}}=\sqrt{\frac{3\pi}{8}}\bar{c}=1.085\bar{c}=\sqrt{\frac{3kT}{m}}=1.732\sqrt{\frac{kT}{m}} \tag{6.7.11}$$

Gauss:

$$f\left(u^{2}\right)=\sqrt{\frac{m}{2\pi kT}}e^{-\frac{mu^{2}}{2kT}}. \tag{6.7.12}$$

Maxwell-Boltzmann:

$$\Phi\left(c^{2}\right)=\sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}c^{2}e^{-\frac{mc^{2}}{2kT}}. \tag{6.7.13}$$

One last thing occurs to me before we leave this section. Can we calculate the *median* speed $c_{1/2}$ of the Maxwell-Boltzmann distribution? This is the speed such that half of the molecules are moving slower than $c_{1/2}$, and half are moving faster. It is the speed that divides the area under the curve in half. If we express speeds in units of c_{m}, we have to find $c_{1/2}$ such that

$$\frac{4}{\sqrt{\pi}}\int_{0}^{c_{1/2}}c^{2}e^{-c^{2}}dc=\frac{1}{2}, \tag{6.7.14}$$

or

$$\int_{0}^{c_{1/2}}c^{2}e^{-c^{2}}dc=\frac{\sqrt{\pi}}{8}=0.2215567314 \tag{6.7.15}$$

That should keep your computer busy for a while. Mine made the answer $c_{1/2} = 1.087\ 65\ c_{\mathrm{m}}$.

6.8: Forces Between Molecules

We described in a qualitative manner in Section 6.3 the forces between molecules – the long-range attractive van der Waals forces caused by induced-dipole/induced-dipole interaction, and the shortrange repulsive Coulomb forces as the molecules approach each other closely, and how these intermolecular forces give rise to deviations from the “Boyle’s Law” expectations for the equation of state for an ideal gas. Presumably, if we knew the exact equation for the force law as a function of intermolecular distance, we could in principle calculate the equation of state; conversely, if we knew, through measurement, the form of the equation of state, we could deduce the form of the intermolecular forces. I have not actually done this myself; an early reference worthwhile to look up would be Lennard-Jones, Proc. Roy, Soc. **A112**, 214, (1926).

Qualitatively, the force law for the interaction between molecules would show a repulsive force rapidly falling off with distance when the molecules are very close (the molecules are “hard”) and a longer-range attractive force at larger distances. Two of the simpler equations that have been used to describe this are the Lennard-Jones potential:

$$V = D\left[1+\left(\frac{r_c}{r}\right)^{12}-2\left(\frac{r_c}{r}\right)^{6}\right] \tag{6.8.1}$$

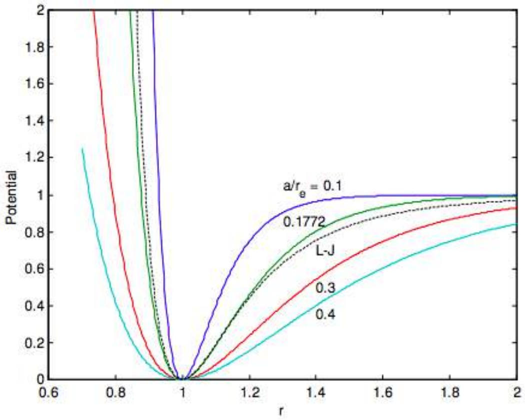
and the Morse potential:

$$V = D\left(1-e^{-(r-r_e)/a}\right)^2 \tag{6.8.2}$$

Each of these goes to V → D as r → ∞, and V = 0 when r = re. The Lennard-Jones potential (but not the Morse potential) goes to ∞ as r → 0.

These expressions cannot be “derived” in the usual sense; they are merely expressions that are useful for discussion in that they describe qualitatively the shape of the potential function that you would expect. The Lennard-Jones expression is often used in discussions of the van der Waals force: if the van der Waals attractive force is due mostly to induced-dipole/induced-dipole interaction, an r^{-6} term is about right. The Morse potential is used more often in discussion of the force between atoms in a bound molecule. If the Morse potential is put into the Schrödinger equation for an anharmonic oscillating diatomic molecule, it results in a simple solution for the eigenfunctions and eigenvalues, with the energy levels being given as quadratic (and no higher) in $v+\frac{1}{2}$.

FIGURE VI.12



The parameter *a* in the Morse expression determines how narrow or how broad the minimum is. It is left as an exercise for the reader to show that the FWHm (full width at half minimum) of the Morse expression is the same as for the Lennard-Jones potential for

$$a = \frac{(2+\sqrt{2})^{1/6}-(2-\sqrt{2})^{1/6}}{\ln(3+\sqrt{8})} = 0.177212908 \tag{6.8.3}$$

In figure VI.12, I show, as continuous curves, the Morse potentials (in order of increasing width) for a/r_e = 0.1, 0.1772, 0.3 and 0.4, and the Lennard-Jones potential as a dashed curve. Further comparisons between these two potential functions can be found in T.-C. Lim, Z. *Naturforschung*, **58a**, 615, (2003).

CHAPTER OVERVIEW

7: The First and Second Laws of Thermodynamics

7.1: The First Law of Thermodynamics, and Internal Energy

The First Law of thermodynamics is:

The **increase** of the *internal energy* of a system is equal to the sum of the *heat* added **to** the system plus the *work* done **on** the system.

In symbols:

$$dU = dQ + dW \tag{7.1.1}$$

You may regard this, according to taste, as any of the following

A fundamental law of nature of the most profound significance;

or A restatement of the law of conservation of energy, which you knew already;

or A recognition that heat is a form of energy.

or A definition of *internal energy*.

Note that some authors use the symbol E for internal energy. The majority seem to use U, so we shall use U here.

Note also that some authors write the first law as $dU = dQ - dW$, so you have to be clear what the author means by dW. A scientist is likely to be interested in what happens **to** a system when you do work **on** it, and is likely to define dW as the work done **on** the system, in which case $dU = dQ + dW$. An engineer, in the other hand, is more likely to be asking how much work can be done **by** the system, and so will prefer dW to mean the work done **by** the system, in which case $dU = dQ - dW$.

The internal energy of a system is made up of many components, any or all of which may be increased when you add heat **to** the system or do work **on** it. If the system is a gas, for example, the internal energy includes the translational, vibrational and rotational kinetic energies of the molecules. It also includes potential energy terms arising from the forces between the molecules, and it may also include excitational energy if the atoms are excited to energy levels above the ground state. It may be difficult to calculate the total internal energy, depending on which forms of energy you take into account. And of course the *potential* energy terms are always dependent on what state you define to have zero potential energy. Thus it is really impossible to define the total internal energy of a system uniquely. What the first law tells us is the *increase* in internal energy of a system when heat is added **to** it and work is done **on** it.

Note that internal energy is a *function of state*. This means, for example in the case of a gas, whose *state* is determined by its pressure, volume and temperature, that the internal energy is uniquely determined (apart from an arbitrary constant) by P, V and T – i.e. by the state of the gas. It also means that in going from one state to another (i.e. from one point in PVT space to another), the change in the internal energy is *route-independent*. The internal energy may be changed by performance of work or by addition of heat, or some combination of each, but, whatever combination of work and energy is added, the change in internal energy depends only upon the initial and final states. This means, mathematically, that dU is an *exact differential* (see Chapter 2, Section 2.1). The differentials dQ and dW, however, are *not* exact differentials.

Note that if work is done on a Body by forces in the Rest of the Universe, and heat is transferred to the Body from the Rest of the Universe (also known as the Surroundings of the Body), the internal energy of the Body increases by $dQ + dW$, while the internal energy of the Rest of the Universe (the Surroundings) decreases by the same amount. Thus the internal energy of the Universe is constant. This is an equivalent statement of the First Law. It is also sometimes stated as “Energy can neither be created nor destroyed”.

7.2: Work

There are many ways in which you can do work **on** a system. You may compress a gas; you may magnetize some iron; you may charge a battery; you may stretch a wire, or twist it; you may stir a beaker of water.

Some of these processes are *reversible*; others are irreversible or dissipative. The work done in compressing a gas is reversible if it is quasistatic, and the internal and external pressures differ from each other always by only an infinitesimal amount. Charging a lead-acid car battery may be almost reversible; charging or discharging a flashlight battery is not, because it has a high internal resistance, and the chemical reactions are irreversible. Stretching or twisting a wire is reversible as long as you do not exceed the elastic limit. If you do exceed the elastic limit, it will not return to its original length; that is, it exhibits elastic *hysteresis*. When you magnetize a metal sample, you are doing work on it by rotating the little magnetic moments inside the metal. Is this reversible? To answer this, read about the phenomenon of magnetic hysteresis in Chapter 12, Section 12.6, of Electricity and Magnetism.

Work that is reversible is sometimes called *configuration work*. It is also sometimes called PdV work, because that is a common example. Work that is not reversible is sometimes called *dissipative work*. Forcing an electric current through a wire is clearly dissipative.

For much of the time, we shall be considering the work that is done **on** a system by *compressing* it. Solids and liquids require huge pressures to change their volumes significantly, so we shall often be considering a *gas*. We imagine, for example, that we have a quantity of gas held in a cylinder by a piston. The work done in compressing it in a reversible process is $-PdV$. If you are asking yourself "Is P the pressure that the gas is exerting on the piston, or the pressure that the piston is exerting on the gas?", remember that we are considering a reversible and quasistatic process, so that the difference between the two is at all stages infinitesimal. Remember also that in calculus, if x is some scalar quantity, the expression dx doesn't mean vaguely the "change" in x (an ill-defined word), but it means the *increment* or *increase* in x. Thus the symbol dV means the *increase* in volume, which is negative if we are doing work **on** the gas by *compressing* it. In any case whether you adopt the scientist convention or the engineer convention (try both) the first law, when applied to the compression or expansion of a gas, becomes

$$dU = dQ - PdV. \tag{7.2.1}$$

7.3: Entropy

Definition: Entropy Differential

If an infinitesimal quantity of heat dQ is added to a system at temperature T, and if no irreversible work is done on the system, the increase in entropy dS of the system is defined by

$$dS = \frac{dQ}{T}. \tag{7.3.1}$$

Exercise 7.3.1

What are the SI units of entropy?

Note that, since dQ is supposed to be an infinitesimal quantity of heat, any increase in temperature is also infinitesimal. Note also that, as with internal energy, we have defined only what is meant by an *increase* in entropy, so we are not in any position to state what *the* entropy of a system is. (Much later, we shall give evidence that the molar entropy of all substances is the same at the absolute zero of temperature. It may then be convenient to define the zero of the entropy scale as the molar entropy at the absolute zero of temperature. At present, we have not yet shown that there is an absolute zero of temperature, let alone of entropy.)

To the question "What is meant by entropy?" a student will often respond with "Entropy is the state of disorder of a system." What a vague, unquantitative and close to meaningless response that is! What is meant by "disorder"? What could possibly be meant by a statement such as "The state of disorder of this system is 5 joules per kelvin"? Gosh! I would give nought marks out of ten for such a response! Now it *is* true, when we come to the subjects of statistical mechanics, and statistical thermodynamics and mixing theory, that there is a sense in which the entropy of a system is some sort of measure of the state of disorder, in the sense that the more disordered or randomly mixed a system is, the higher its entropy, and random processes do lead to more disorder and to higher entropy. Indeed, this is all connected to the second law of thermodynamics, which we haven't touched upon yet. But please, at the present stage, entropy is defined as I have stated above, and, for the time being, it means nothing less and nothing more.

It will have been noted that, in our definition of entropy so far, we specified that no irreversible work be done on the system. What if some irreversible work *is* done? Let us suppose that we do work on a gas in two ways. (I choose a gas in this discussion, because it is easier to imagine compressing a gas with PdV work than it is with a solid or a liquid, because the compressibility of a solid or a liquid is relatively low. But the same argument applies to any substance.) We compress it with the piston, but, at the same time, we also stir it with a paddle. In that case, the work done **on** the gas is *more* than $-PdV$. (Remember that $-PdV$ is positive.) If we didn't compress it at all, but only stirred it, dV would be zero, but we would still have done work on the gas by stirring. Let's suppose the work done on the gas is

$$\delta W = -PdV + \delta W_{irr}. \tag{7.3.2}$$

The part δW_{irr} is the irreversible or dissipative part of the work done **on** the gas; it is unrecoverable as work, and is *irretrievably* converted to heat. You cannot use it to turn the paddle back. Nor can you cool the gas by turning the paddle backwards.

We can now define the increase of entropy in the irreversible process by

$$TdS = dQ + dW_{irr} \tag{7.3.3}$$

that is,

$$dS = \frac{dQ + dW_{\text{irr}}}{T}. \tag{7.3.4}$$

In other words, since dW_{irr} is irreversibly converted to heat, it is just as though it were part of the addition of heat.

In summary,

$$dU = dQ + dW \tag{7.3.5}$$

and

$$dU = TdS - PdV \tag{7.3.6}$$

apply whether there is reversible or irreversible work. But only if there is no irreversible (unrecoverable) work does $dQ = TdS$ and $dW = -PdV$. If there is any irreversible work,

$$dW = -PdV + dW_{irr} \tag{7.3.7}$$

and

$$dQ = TdS - dW_{irr}. \tag{7.3.8}$$

Of course there are other forms of reversible work than PdV work; we just use the expansion of gases as a convenient example.

Note that P, V, and T are state variables (together, they define the state of the system) and U is a function of state. Thus the *entropy*, too, is a *function of state*. That is to say that the change in entropy as you go from one point in *PVT*-space to another point is route-independent. If you return to the same point that you started at (the same state, the same values of P, V and T), there is no change in entropy, just as there is no change in internal energy.

Definition: Specific Heat Capacity

The *specific heat capacity* C of a substance is the quantity of heat required to raise the temperature of unit mass of it by one degree. We shall return to the subject of heat capacity in Chapter 8. For the present, we just need to know what it means, in order to do the following exercise concerning entropy.

Example 7.3.1

A litre (mass = 1 kg) of water is heated from 0 $^{\text{o}}$C to 100 $^{\text{o}}$C. What is the increase of entropy? Assume that the specific heat capacity of water is *C* = 4184 J kg^{-1} K^{-1}, that it does not vary significantly through the temperature range of the question, and that the water does not expand significantly, so that no significant amount of work (reversible or irreversible) is done.

Solution

The heat required to heat a mass m of a substance through a temperature range dT is $mCdT$. The entropy gained then is $\frac{mCdT}{T}$. The entropy gained over a finite temperature range is therefore

$$\begin{aligned} mC\int_{T_i}^{T_2}\frac{dT}{T} &= mC\ln\left(\frac{T_2}{T_1}\right) \\ &= 1\times 4184\times\ln\left(\frac{373.15}{273.15}\right) = 1305\text{ JK}^{-1}. \end{aligned}$$

7.4: The Second Law of Thermodynamics

In a famous lecture entitled *The Two Cultures* given in 1959, the novelist C. P. Snow commented on a common intellectual attitude of the day - that true education consisted of familiarity with the humanities, literature, arts, music and classics, and that scientists were mere uncultured technicians and ignorant specialists who never read any of the great works of literature. He described how he had often been provoked by such an attitude into asking some of the self-proclaimed intellectuals if they could describe the Second Law of Thermodynamics – a question to which he invariably received a cold and negative response. Yet, he said, he was merely asking something of about the scientific equivalent of "Have you read a work of Shakespeare?"

So I suggest that, if you have never read a work of Shakespeare, take a break for a moment from thermodynamics, go and read *A Midsummer Night's Dream*, and come back refreshed and ready to complete your well-rounded education by learning the Second Law of Thermodynamics.

We have defined entropy in such a manner that if a quantity of heat dQ is added reversibly to a system at temperature T, the increase in the entropy of the system is $dS = dQ/T$. We also pointed out that if the heat is transferred *irreversibly*, $dS > dQ/T$.

Now consider the following situation (figure VII.1).

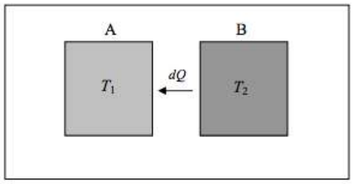


FIGURE VII.1

An isolated system consists of two bodies, A at temperature T_1 and B at temperature T_2, such that $T_2 > T_1$. Heat will eventually be exchanged between the two bodies, and on the whole more heat will be transferred from B to A than from A to B. That is, there will be a *net* transference of heat, dQ, from B to A. Perhaps this heat is transferred by radiation. Each body is sending forth numerous photons of energy, but there is, on the whole, a net flow of photons from B to A. Or perhaps the two bodies are in contact, and heat is being transferred by conduction. The vibrations in the hot body are more vigorous than those in the cool body, so there will be a net transfer of heat from B to A. However, since the emission of photons in the first case, and the vibrations in the second place, are random, it will be admitted that it is not impossible that at some time more photons may move from A to B than from B to A. Or, in the case of conduction, most of the atoms in A happen to be moving to the right while only a few atoms in B are moving to the left in the course of their oscillations. But, while admitting that this is in principle possible and not outside the laws of physics, it is exceedingly unlikely to happen in practice; indeed so unlikely as hardly to be taken seriously. Thus, in any natural, spontaneous process, without the intervention of an External Intelligence, it is almost certain that there will be a net transfer of heat from B to A. And this process, barring the most unlikely set of circumstances, is irreversible.

The hot body will *lose* an amount of entropy dQ/T_2, while the cool body will gain an amount of entropy dQ/T_1, which is greater than dQ/T_2. Thus the entropy of the isolated system as a whole increases by $dQ/T_1 - dQ/T_2$.

From this argument, we readily conclude that *any natural, spontaneous and irreversible thermodynamical processes taking place within an isolated system are likely to lead to an increase in entropy of the system*. This is perhaps the simplest statement of the *Second Law of Thermodynamics*.

I have used the phrase "is likely to", although it will be realised that in practice the possibility that the entropy might decrease in a natural process is so unlikely as to be virtually unthinkable, even though it could in principle happen without violating any fundamental laws of physics.

You could regard the Universe as an isolated system. Think of a solid Body sitting somewhere in the Universe. If the Body is hot, it may spontaneously lose heat to the Rest of the Universe. If it is cold, it may spontaneously absorb heat from the Rest of the Universe. Either way, during the course of a spontaneous process, the entropy of the Universe increases.

The transference of heat from a hot body to a cooler body, so that both end at the same intermediate temperature, involves, in effect, the mixing of a set of fast-moving molecules and a set of slow-moving molecules. A similar situation arises if we start with a box having a partition down the middle, and on one side of the partition there is a gas of blue molecules and on the other there is a gas of red molecules. If we remove the partition, eventually the gases will mix into one homogeneous gas. By only a slight extension of the idea of entropy discussed in courses in statistical mechanics, this situation can be described as an increase of entropy – called, in fact, the entropy of mixing. If you saw two photographs, in one of which the blue and red molecules were separated, and in the other the two colours were thoroughly mixed, you would conclude that the latter photograph was probably taken later than the former. But only "probably"; it is conceivable, within the laws of physics, that the velocities of the blue and red molecules separated themselves out without external intervention. This would be allowed perfectly well within the laws of physics. Indeed, if the velocities of all the molecules in the mixed gases were to be reversed, the gases would eventually separate into their two components. But this would seem to be so unlikely as never in practice to happen. The second law says that the entropy of an isolated system is *likely* (*very* likely!) to increase with time. Indeed it could be argued that the increase of entropy is the criterion that defines the direction of the arrow of time. (For more on the arrow of time, see Section 15.12 of the notes on Electricity and Magnetism of this series. Also read the article on the *arrow of time* by Paul Davis, *Astronomy & Geophysics* (Royal Astronomical Society) **46**, 26 (2005). You'll probably also enjoy H. G. Wells's *The Time Machine*.)

Note that, in the example of our two bodies exchanging heat, one *loses* entropy while the other *gains* entropy; but the gain by the one is greater than the loss from the other, with the result that there is an *increase* in the entropy *of the system as a whole*. The principle of the increase of entropy applies to an *isolated* system.

In case you have ever wondered (who hasn't?) how life arose on Earth, you now have a puzzle. Surely the genesis and subsequent evolution of life on Earth represents an increase in order and complexity, and hence a *decrease in the entropy of mixing*. You may conclude from this that the genesis and subsequent evolution of life on Earth requires Divine Intervention, or Intelligent Design, and that the Second Law of Thermodynamics provides Proof of the Existence of God. Or you may conclude that Earth is not an isolated thermodynamical system. Your choice.

CHAPTER OVERVIEW

8: Heat Capacity, and the Expansion of Gases

8.1: Heat Capacity

Definition: The heat capacity of a body is the quantity of heat required to raise its temperature by one degree. Its SI unit is J K^{-1}.

Definition: The specific heat capacity of a substance is the quantity of heat required to raise the temperature of unit mass of it by one degree. Its SI unit is J kg^{-1} K^{-1}.

Definition: The molar heat capacity of a substance is the quantity of heat required to raise the temperature of a molar amount of it by one degree. (I say "molar amount". In CGS calculations we use the mole – about 6 × 10^{23} molecules. In SI calculations we use the kilomole – about 6 × 10^{26} molecules.) Its SI unit is J $kilomole^{-1}$ K^{-1}.

Some numerical values of specific and molar heat capacity are given in Section 8.7.

One sometimes hears the expression "the specific heat" of a substance. One presumes that what is meant is the specific heat capacity.

The above definitions at first glance seem easy to understand – but we need to be careful. Let us imagine again a gas held in a cylinder by a movable piston. I choose a gas because its volume can change very obviously on application of pressure or by changing the temperature. The volume of a solid or a liquid will also change, but only by a small and less obvious amount. If you supply heat to a gas that is *allowed to expand at constant pressure*, some of the heat that you supply goes to doing external work, and only a part of it goes towards raising the temperature of the gas. On the other hand, *if you keep the volume of the gas constant*, all of the heat you supply goes towards raising the temperature. Consequently, more heat is required to raise the temperature of the gas by one degree if the gas is allowed to expand at constant pressure than if the gas is held at constant volume and not allowed to expand. Thus the heat capacity of a gas (or any substance for that matter) is greater if the heat is supplied at constant pressure than if it is supplied at constant volume. Thus we have to distinguish between the *heat capacity at constant volume* C_V and the *heat capacity at constant pressure* C_P, and, as we have seen $C_P > C_V$.

If the heat is added at constant volume, we have simply that $dU = dQ = C_V dT$.

One other detail that requires some care is this. The specific heat capacity of a substance may well vary with temperature, even, in principle, over the temperature range of one degree mentioned in our definitions. Therefore, we really have to define the heat capacity at a given temperature in terms of the heat required to raise the temperature by an infinitesimal amount rather than through a finite range. Thus it is perhaps easiest to **define** heat capacity at constant volume in symbols as follows:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{8.1.1}$$

(Warning: Do not assume that $C_P = (\partial U/\partial T)_P$. That isn't so. The correct expression is given as equation 9.1.13 in Chapter 9 on Enthalpy.)

As with many equations, this applies equally whether we are dealing with total, specific or molar heat capacity or internal energy.

If heat is supplied at constant pressure, some of the heat supplied goes into doing external work PdV, and therefore

$$C_p dT = C_V dT + PdV. \tag{8.1.2}$$

For a mole of an *ideal gas* at *constant pressure*, $P\,dV = R\,dT$, and therefore, for an ideal gas,

$$C_p = C_v + R, \tag{8.1.3}$$

where, in this equation, C_P and C_V are the molar heat capacities of an ideal gas.

We shall see in Chapter 10, Section 10.4, if we can develop a more general expression for the difference in the heat capacities of *any* substance, not just an ideal gas. But let us continue, for the time being with an ideal gas.

In an ideal gas, there are no forces between the molecules, and hence no potential energy terms involving the intermolecular distances in the calculation of the internal energy. In other words, the internal energy is independent of the distances between molecules, and hence the internal energy is independent of the volume of a fixed mass of gas if the temperature (hence kinetic energy) is kept constant. That is, for an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{8.1.4}$$

Let us think now of a *monatomic* gas, such as helium or argon. When we supply heat **to** (and raise the temperature of) an ideal monatomic gas, we are increasing the translational kinetic energy of the molecules. If the gas is *ideal*, so that there are no intermolecular forces then *all* of the introduced heat goes into increasing the translational kinetic energy (i.e. the temperature) of the gas. (Recall that a gas at low pressure is nearly ideal, because then the molecules are so far apart that any intermolecular forces are negligible.) Recall from Section 6.5 that the translational kinetic energy of the molecules in a mole of gas is $\frac{3}{2}RT$. The molar internal energy, then, of an ideal monatomic gas is

$$U=\frac{3}{2}RT+\text{constant}. \tag{8.1.5}$$

From equation 8.1.1, therefore, the molar heat capacity at constant volume of an ideal monatomic gas is

$$C_V=\frac{3}{2}R. \tag{8.1.6}$$

The molar heat capacities of real monatomic gases when well above their critical temperatures are indeed found to be close to this.

When we are dealing with *polyatomic* gases, however, the heat capacities are greater. This is because, when we supply heat, only some of it goes towards increasing the translational kinetic energy (temperature) of the gas. Some of the heat goes into increasing the *rotational* kinetic energy of the molecules. (Wait! Some of you are asking yourselves: "But do not atoms of helium and argon rotate? Do they not have rotational kinetic energy?" These are very good questions, but I am going to pretend for the moment that I haven't heard you. Perhaps, before I come to the end of this section, I may listen.)

When two molecules collide head on, there is an interchange of translational kinetic energy between them. But if they have a glancing collision, there is an exchange of translational and rotational kinetic energies. If millions of molecules are colliding with each other, there is a constant exchange of translational and rotational kinetic energies. When a dynamic equilibrium has been established, the kinetic energy will be shared equally between each degree of translational and rotational kinetic energy. (This is the *Principle of Equipartition of Energy*.) We know that the translational kinetic energy per mole is $\frac{3}{2}RT$ - that is, $\frac{1}{2}RT$ for each translational *degree of freedom* (\frac{1}{2} m \overline{u}^{2}, \frac{1}{2} m \overline{v^{2}}, \frac{1}{2} m \overline{w^{2}}\)). There is an equal amount of kinetic energy of rotation (with an exception to be noted below), so that the internal energy associated with a mole of a polyatomic gas is 3*RT* plus a constant, and consequently the molar heat capacity of an ideal *polyatomic* gas is

$$C_V=3R. \tag{8.1.7}$$

It takes twice the heat to raise the temperature of a mole of a polyatomic gas compared with a monatomic gas.

The exception we mentioned is for *linear* molecules. These are molecules in which all the atoms are in a straight line. This necessarily includes, of course, all diatomic molecules (the oxygen and nitrogen in the air that we breathe) as well as some heavier molecules such as CO2, in which all the molecules (at least in the ground state) are in a straight line. (The molecule H2O is not linear.) In linear molecules, the moment of inertia about the internuclear axis is negligible, so there are only two degrees of rotational freedom, corresponding to rotation about two axes perpendicular to each other and to the internuclear axis. Thus there are five degrees of freedom in all (three of translation and two of rotation) and the kinetic energy associated with each degree of freedom is $\frac{1}{2}RT$ per mole for a total of $\frac{5}{2}RT$ per mole, so the molar heat capacity is

$$C_V=\frac{5}{2}R. \tag{8.1.8}$$

Summary: A monatomic gas has three degrees of translational freedom and none of rotational freedom, and so we would expect its molar heat capacity to be $\frac{3}{2}RT$.

A diatomic or linear polyatomic gas has three degrees of translational freedom and two of rotational freedom, and so we would expect its molar heat capacity to be $\frac{5}{2}RT$.

A nonlinear polyatomic gas has three degrees of translational freedom and three of rotational freedom, and so we would expect its molar heat capacity to be 3*R*.

How do real gases behave compared with these predictions? The monatomic gases (helium, neon, argon, etc) behave very well. The diatomic gases quite well, although at room temperature the molar heat capacities of some of them are a little higher than predicted, while at low temperatures the molar heat capacities drop below what is predicted. Indeed below about 60 K the molar heat capacity of hydrogen drops to about $\frac{3}{2}RT$ - just as if it had become a monatomic gas or, though still diatomic, the molecules were somehow prevented from rotating. The molar heat capacities of nonlinear polyatomic molecules tend to be rather higher than predicted.

First let us deal with why the molar heat capacities of polyatomic molecules and some diatomic molecules are a bit higher than predicted. This is because the molecules may *vibrate*. When we add heat, some of the heat is used up in increasing the rate of rotation of the molecules, and some is used up in causing them to vibrate, so it needs a lot of heat to cause a rise in temperature (translational kinetic energy). The possibility of vibration adds more degrees of freedom, and another $\frac{1}{2}RT$ to the molar heat capacity for each extra degree of vibration. To be strictly correct, the "number of degrees of freedom" in this connection is the number of squared terms that contribute to the internal energy. Each vibrational mode adds two such terms – a kinetic energy term and a potential energy term. This means that the predicted molar heat capacity for a nonrigid diatomic molecular gas would be $\frac{7}{2}RT$. Polyatomic gases have many vibrational modes and consequently a higher molar heat capacity.

So – why is the molar heat capacity of molecular hydrogen not $\frac{7}{2}RT$ at all temperatures? Why is it about $\frac{5}{2}RT$ at room temperature, as if it were a rigid molecule that could not vibrate? True, at higher temperatures the molar heat capacity does increase, though it never quite reaches $\frac{7}{2}RT$ before the molecule dissociates. Why does the molar heat capacity decrease at lower temperatures, reaching $\frac{3}{2}RT$ at 60 K, as if it could no longer rotate?

Let us ask some further questions, which are related to these. We said earlier that a monatomic gas has no rotational degrees of freedom. Why not? True, the moment of inertia is very small, but, if we accept the principle of equipartition of energy, should not each rotational degree of freedom hold as much energy as each translational degree of freedom? Also, we said that a linear molecule has just two degrees of freedom. It is true that the moment of inertia about the internuclear axis is very small. This is not the same thing as saying that it cannot rotate about that axis. If all degrees of freedom equally share the internal energy, then the angular speed about the internuclear axis must be correspondingly large.

Now I could make various excuses about these problems. The fact is, however, that the classical model that I have described may look good at first, but, when we start asking these awkward questions, it becomes evident that the classical theory really fails to answer them satisfactorily. In truth, the failure of classical theory to explain the observed values of the molar heat capacities of gases was one of the several failures of classical theory that helped to give rise to the birth of quantum theory. Quantum theory in fact accounts spectacularly well and in detail for the specific heat capacities of molecules and how the heat capacities vary with temperature. This topic is often dealt with on courses on statistical thermodynamics, and I just briefly mention the explanation here. The solution of Schrödinger's equation for a rigid rotator shows that the rotational energy can exist with a number of separated discrete values, and the population of these rotational energy levels is governed by Boltzmann's equation in just the same way as the population of the electronic energy levels in an atom. At temperatures of 60 K, the spacing of the rotational energy levels is large compared with kT, and so the rotational energy levels are unoccupied. Thus, in that very real sense, the hydrogen molecule does indeed stop rotating at low temperatures. The spacing of the energy level is inversely proportional to the moment of inertia, and the moment of inertia about the internuclear axis is so small that the energy of the first rotational energy level about this axis is larger than the dissociation energy of the molecule, so indeed the molecule cannot rotate about the internuclear axis. Vibrational energy is also quantised, but the spacing of the vibrational levels is much larger than the spacing of the rotational energy levels, so they are not excited at room temperatures. This has been only a brief account of why classical mechanics fails and quantum mechanics succeeds in correctly predicting the observed heat capacities of gases. It is a very interesting subject, and the reader may well want to learn more about it – but that will have to be elsewhere.

8.2: Ratio of the Heat Capacities of a Gas

The ratio of the heat capacities of a gas at constant pressure and at constant volume plays an important part in many calculations involving the expansion and contraction of gases. The ratio appears, for one example of many that could be chosen, in the theoretical expression for the speed of sound in a gas. The higher the ratio C_P/C_V, the faster the speed of sound. The ratio is generally given the symbol γ:

$$\frac{C_p}{C_v} = \gamma. \tag{8.2.1}$$

Apart from any other reason, one reason for its importance is that the ratio is easier to measure precisely than either heat capacity separately. For example, you could determine it from a measurement of the speed of sound, which is easier than adding heat to a sample of gas at constant pressure and again at constant volume and measuring the rise in temperature.

We have seen that, for gases that behave as we would like them to behave, the molar heat capacities C_V at constant temperatures for monatomic, diatomic and nonlinear polyatomic gases without molecular vibration are respectively $\frac{3}{2}R$, $\frac{5}{2}R$, and $3R$. And since, for an ideal gas, $C_P = C_V + R$, (equation 8.1.3), we expect the corresponding values for C_P to be $\frac{5}{2}R$, $\frac{7}{2}R$ and $4R$. and Thus the expected values of γ are 5/3, 7/5 and 4/3.

8.3: Isothermal Expansion of an Ideal Gas

An ideal gas obeys the equation of state $PV = RT$ (V = molar volume), so that, if a fixed mass of gas kept at constant temperature is compressed or allowed to expand, its pressure and volume will vary according to PV = constant. That is, Boyle's Law. We can calculate the *work done* **by** a mole of an ideal gas in a reversible isothermal expansion from volume V_1 to volume V_2 as follows.

$$W=\int_{V_1}^{V_2} PdV = RT\int_{V_1}^{V_2}\frac{dV}{V} = RT\ln(V_2/V_1) \tag{8.3.1}$$

8.4: Reversible Adiabatic Expansion of an Ideal Gas

An adiabatic process is one in which no heat enters or leaves the system, and hence, for a reversible adiabatic process the first law takes the form $dU = -PdV$. But from equation 8.1.1, $C_V = (\partial U/\partial T)_V$. But the internal energy of an ideal gas depends only on the temperature and is independent of the volume (because there are no intermolecular forces), and so, for an ideal gas, $C_V = dU/dT$, and so we have $dU = C_V dT$. Thus for a reversible adiabatic process and an ideal gas, $C_V dT = -PdV$. (The minus sign shows that as V increases, T decreases, as expected.) But for a mole of an ideal gas, $PV = RT = (C_P - C_V)T$, or $P = (C_P - C_V)T/V$.

Therefore

$$C_v dT = -(C_P - C_V)\, T dV/V \tag{8.4.1}$$

(You may be wondering whether C and V are molar, specific or total quantities. If you look at the equation you'll agree that it is valid whether the volume and heat capacities are molar, specific or total.)

Separate the variables and write γ for C_P/C_V:

$$\frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0. \tag{8.4.2}$$

Integrate:

$$TV^{\gamma-1} = \text{constant}\,. \tag{8.4.3}$$

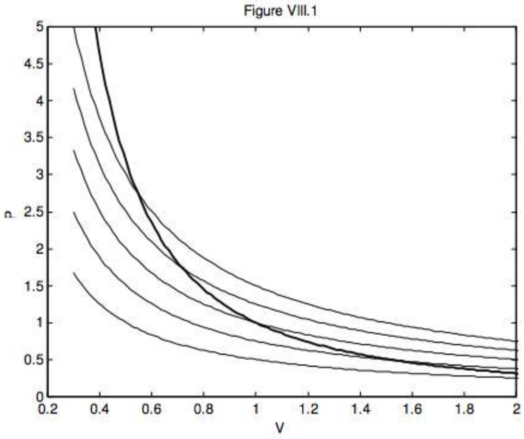
This shows how temperature and volume of an ideal gas vary during a reversible adiabatic expansion or compression. If the gas expands, the temperature goes down. If the gas is compressed, it becomes hot. Of course the pressure varies also, and the ideal gas conforms to the equation PV/T = constant. On elimination of T we obtain

$$PV^{\gamma} = \text{constant}\,. \tag{8.4.4}$$

On elimination of V we obtain

$$P^{-(\gamma-1)}T^{\gamma} = \text{constant}. \tag{8.4.5}$$

In figure VIII.1 I draw, as light curves, five isotherms – i.e. the paths that would be taken by an ideal gas in the PV plane in isothermal processes at five temperatures. I also show, as a heavier line, an *adiabat*, PV^{γ} = constant , which I calculated for $\gamma = 5/3$. The adiabat is steeper than the isotherms, and the curve shows that, as the gas expands adiabatically, the temperature drops. If you know the original temperature and the old and new volumes, equation 8.4.3 will enable you to calculate the new temperature. If you know the original temperature and the old and new pressures, equation 8.4.5 will enable you to calculate the new temperature. While these purely thermodynamic arguments show that a gas becomes hotter if you compress it, this is also to be expected at the microscopic level. Thus, if a molecule bounces elastically against a piston that is moving towards it, it will gain kinetic energy, and it will lose kinetic energy if it bounces off a piston that is moving away from it.



Let us calculate the work done by a mole of an ideal gas in a reversible adiabatic expansion from (P_1, V_1) to (P_2, V_2):

$$W = \int_{V_1}^{V_2} P dV. \tag{8.4.6}$$

For a reversible adiabatic expansion, $PV^\gamma = K$, and therefore

$$W = K\int_{v_1}^{v_2} V^{-\gamma} dV = \frac{K}{\gamma - 1}\left(V_1^{-(\gamma-1)} - V_2^{-(\gamma-1)}\right) \tag{8.4.7}$$

That is,

$$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1} = \frac{R(T_1 - T_2)}{\gamma - 1} \tag{8.4.8}$$

(Note that $T_2 < T_1$ in this adiabatic expansion.)

Compare this with equation 8.3.1 for an isothermal expansion.

Note also that, since $R = C_P - C_V$ and $C_P/C_V = \gamma$ this can also be written

$$W = C_V (T_1 - T_2) \tag{8.4.9}$$

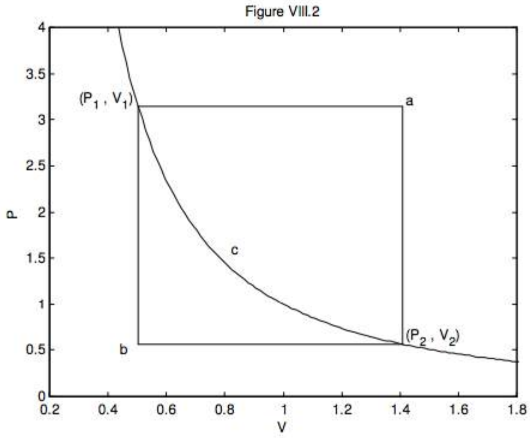
This is also equal to the heat that would be lost if the gas were to cool from T1 to T2 at constant volume. Think about this! Is it coincidence, or must it be so?

Here is a useful *exercise*. In figure VIII.2, a gas goes from (P_1, V_1) to (P_2, V_2) via three different reversible routes:

(a) An isobaric expansion followed by an isochoric decrease in pressure;

(b) An isochoric decrease in pressure followed by an isobaric expansion;

(c) An adiabatic expansion.



At each stage, calculate the work done **on** or **by** the gas, the heat gained **by** the gas or lost **from** the gas, and the **increase** or **decrease** of the internal energy of the gas. This exercise will illustrate that U is a function of state, but Q and W are not. (I expect the answers to be in algebra; ignore the numbers on the axes – they don't mean anything in particular.)

8.5: The Clément-Desormes Experiment

This is a simple, quick and effective experiment often seen in teaching laboratories for measuring γ for air, or, with some extra effort, any other gas.

Sometimes this experiment is referred to as the experiment of Clément and Desormes, and sometimes as the experiment of Clément-Desormes. Apparently Charles-Bernard Desormes was the uncle of Nicolas Clément, and they both worked on the experiment. Nicolas Desormes later legally changed his name to Nicolas Clément-Desormes. Thus you can refer either to the experiment of Clément and Desormes or to the experiment of Clément-Desormes!

A bottle of air starts at P_1, T_1. P_1 is a little greater than atmospheric pressure P_0. T1 is the ambient room temperature. The bottle is provided with some device for measuring pressure (for example, a manometer). We'll see that there is no need to measure temperatures. The stopcock is quickly opened and immediately closed. The pressure at that moment is just atmospheric pressure, which I'll call P_0, and the temperature is T_2, which is a little cooler than the original room temperature T1. The bottle of gas is now allowed slowly to warm up isochorically to its original temperature T_1, by which time the new pressure P_2 is greater than atmospheric pressure P_0 but not as large as the original pressure P_1. You should sketch these two stages on a *PV* diagram.

For the adiabatic process,

$$P_1^{-(\gamma-1)}T_1^{\gamma} = P_0^{-(\gamma-1)}T_2^{\gamma}. \tag{8.5.1}$$

For the isochoric process,

$$P_0/T_2 = P_2/T_1. \tag{8.5.2}$$

I'll leave you to do the algebra and eliminate T_2/T_1 from these equations and hence show that

$$\gamma = \frac{\ln(P_1/P_0)}{\ln(P_1/P_2)}. \tag{8.5.3}$$

In the above analysis, we assumed that the gas was ideal and the expansion was adiabatic and reversible. The gas is nearly ideal if it is a long way above its critical temperature and there are no enormous ranges of P and T. The expansion is adiabatic if P_2 is measured immediately after the stopcock is opened and closed, so that there is no time for heat to enter or leave the system. It is reversible only if $P_1 - P_0 << P_0$. If you want to do the experiment yourself right now without getting up from your comfortable seat, have a look at http://www.univ-lemans.fr/enseignements/physique/02/thermo/clement.html

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8.6: The Slopes of Isotherms and Adiabats

For an ideal gas in an isothermal process, PV = constant.

In a reversible adiabatic process:

PV^{γ} = constant,

$TV^{\gamma} - 1$ = constant,

$P^{1-\gamma}T^{\gamma}$ = constant.

From these it is easy to see that the ratios of the adiabatic, isothermal, isobaric and isochoric slopes are as follows:

$$\left(\frac{\partial P}{\partial V}\right)_S = \gamma\left(\frac{\partial P}{\partial V}\right)_T; \qquad \left(\frac{\partial V}{\partial T}\right)_S = -\frac{1}{\gamma-1}\left(\frac{\partial V}{\partial T}\right)_P; \qquad \left(\frac{\partial P}{\partial T}\right)_S = \frac{\gamma}{\gamma-1}\left(\frac{\partial P}{\partial T}\right)_V. \tag{8.6.1}$$

For example: - isothermal: PV = constant. Take logarithms and differentiate: $\frac{dP}{P}+\frac{dV}{V}=0$. Hence $\left(\frac{\partial P}{\partial V}\right)_T=-\frac{P}{V}$. adiabatic: PV^{γ} = constant. Take logarithms and differentiate: $\frac{dP}{P}+\gamma\frac{dV}{V}=0$. Hence $\left(\frac{\partial P}{\partial V}\right)_S=-\gamma\frac{P}{V}$. The other two relations can be obtained in a similar manner.

Do these relations hold in general for any equation of state, or are they valid only for an ideal gas? In this section, we shall see that they are valid in general for any equation of state, and are not restricted to the equation of state for an ideal gas.

Let us imagine that the state of the working substance (be it gas, liquid or solid) starts in PVT space at point A (P, V, T_A). We are going to take it to a new point B ($P + \delta P$, $V + \delta V$, T_B). As I have drawn it in Figure VIII.3, δP is positive, δV is negative, and $T_B > T_A$.

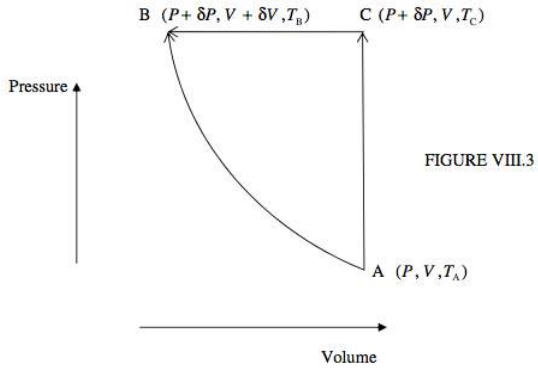


FIGURE VIII.3

We first suppose that we make this move by a *single*, *adiabatic* process. In that case no heat is added to or lost from the system, and the increase in the internal energy is $-P\delta V$.

Alternatively, B can be reached in two stages:

An isochoric path from A to a new point C ($P + \delta P$, V, T_C), followed by

An isobaric path from C to B.

As I have drawn it in Figure VIII.3, $T_C > T_B > T_A$.

In the *isochoric process*, no work is done by or on the system, and *the increase in the internal energy is equal to the heat added to the system*, C_V ($T_C - T_A$).

In the *isobaric process, the increase in the internal energy is equal to the work done on the system*, $-P\delta V$, *minus the heat lost from the system*, C_P ($T_C - T_B$); *that is*, $-C_P$ ($T_C - T_B$) $- P\delta V$.

Therefore, since the total increase in internal energy is route-independent,

$$-P\delta V = C_V(T_c - T_A) - C_P(T_C - T_B) - P\delta V. \tag{8.6.2}$$

Cancel $P\delta V$ and write γ for C_P/C_V, so that

$$(T_{\rm C}-T_{\rm A})=\gamma\,(T_{\rm C}-T_{\rm B})\,. \tag{8.6.3}$$

But $T_{\rm C}=T_{\rm A}+\left(\frac{\partial T}{\partial P}\right)_V\delta P$ and $T_{\rm B}=T_{\rm C}+\left(\frac{\partial T}{\partial V}\right)_P\delta V$.

[Reminder: Here δP means $P_{\rm C}-P_{\rm A}$ (which, in the way in which I have drawn it in figure VIII.3, is positive) and δV means $V_{\rm B}-V_{\rm C}$ (which, in the way in which I have drawn it in figure VIII.3, is negative).]

Therefore

$$\left(\frac{\partial T}{\partial P}\right)_V\delta P=-\gamma\left(\frac{\partial T}{\partial V}\right)_P\delta V. \tag{8.6.4}$$

Divide both sides by δV and go to the infinitesimal limit, recalling that δP and δV are related through an adiabatic path:

$$\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_S=-\gamma\left(\frac{\partial T}{\partial V}\right)_P. \tag{8.6.5}$$

Therefore

$$\left(\frac{\partial P}{\partial V}\right)_S=-\gamma\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial P}{\partial T}\right)_V. \tag{8.6.6}$$

But $\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T=-1$, so $\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial P}{\partial T}\right)_V=-\left(\frac{\partial P}{\partial V}\right)_T$.

Therefore

$$\left(\frac{\partial P}{\partial V}\right)_S=\gamma\left(\frac{\partial P}{\partial V}\right)_T. \tag{8.6.7}$$

Thus, as for the ideal gas, the slope of the adiabat is γ times the slope of the isotherm, only this time we have made no assumption about the equation of state.

The other two relations (equations 8.6.1 b,c) can be dealt with as follows.

Equation 8.6.3 can be rearranged to read

$$T_{\rm B}-T_{\rm A}=-(\gamma-1)\,(T_{\rm B}-T_{\rm C}) \tag{8.6.8}$$

But $T_{\rm B}=T_{\rm A}+\left(\frac{\partial T}{\partial V}\right)_S\delta V$ and $T_{\rm B}=T_{\rm C}+\left(\frac{\partial T}{\partial V}\right)_P\delta V$.

Hence

$$\left(\frac{\partial V}{\partial T}\right)_S=-\frac{1}{\gamma-1}\left(\frac{\partial V}{\partial T}\right)_P, \tag{8.6.9}$$

which is the same as equation 8.6.1 b, but without any assumption about the equation of state.

Note also that

$$\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V=-1. \tag{8.6.10}$$

Combine this with equations 8.6.7 and 8.6.9 to obtain

$$\frac{1}{\gamma}\left(\frac{\partial P}{\partial V}\right)_S(\gamma-1)\left(\frac{\partial V}{\partial T}\right)_S\left(\frac{\partial T}{\partial P}\right)_V=1. \tag{8.6.11}$$

Therefore

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{\gamma-1}{\gamma}\left(\frac{\partial P}{\partial V}\right)_S\left(\frac{\partial V}{\partial T}\right)_S=\frac{\gamma-1}{\gamma}\left(\frac{\partial P}{\partial T}\right)_S. \tag{8.6.12}$$

Therefore

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{\gamma}{\gamma - 1}\left(\frac{\partial P}{\partial T}\right)_V, \tag{8.6.13}$$

which is the same as equation 8.6.1 c, but without any assumption about the equation of state.

8.7: Scale Height in an Isothermal Atmosphere

The material in this chapter doubtless has countless applications, most of which I am unaware of, in meteorology. Two simple topics are easy to mention, namely the *scale height in an isothermal atmosphere*, dealt with in this section, and the adiabatic lapse rate dealt with in the next section.

Let us imagine a column of air of cross-sectional area A in an isothermal atmosphere – that is to say the temperature T is uniform throughout. Consider the equilibrium of the portion of the air between heights z and $z + dz$. The weight of this portion is $\rho gAdz$. Let P be the pressure at height z and $P + dP$ be the pressure at height $z + dz$. (Note that dP is negative.) The net upward force on the portion dz of the air is $-AdP$. Therefore $dP = -\rho gdz$. But if we regard air as an ideal gas, it obeys the equation of state for an ideal gas, equation 6.1.7: $P = \rho RT/\mu$ where ρ and μ are respectively the density and the "molecular weight" (molar mass) of the gas. Therefore $\frac{RT}{\mu}d\rho = -\rho gdz$, or $\frac{d\rho}{\rho} = -\frac{\mu g}{RT}dz$. Integrate to obtain

$$\rho = \rho e^{-z/H} \tag{8.7.1}$$

where $H = \frac{RT}{\mu g}$ is the *scale height*. It is large if the temperature is high, the gas light and the planet's gravity feeble. It is the height at which the density is reduced to a fraction $1/e$, or 36.8%. of its ground value. What would it be, in kilometres, for an atmosphere consisting of 80% N_2 and 20% O_2, at a temperature of 20 ºC, where the gravitational acceleration is 9.8 m s^{-2}? What fraction is this of the radius of Earth? If you made a model of Earth one metre in diameter (radius = 50 cm), how thick would be the atmosphere? You'd better look after it - our atmosphere is a very thin skin clinging to the surface!

8.8: Adiabatic Lapse Rate

Earth's atmosphere is not, of course, isothermal. The temperature decreases with height. The temperature lapse rate in an atmosphere is the rate of decrease of temperature with height; that is to say, it is $-dT/dz$.

An *adiabatic* atmosphere is one in which P/ρ^γ does not vary with height. In such an atmosphere, if a lump of air is moved adiabatically to a higher level, its pressure and density will change so that P/ρ^γ is constant – and will be equal to the ambient pressure and density at the new height. For such an atmosphere, it is possible to calculate the rate at which temperature decreases with height – the *adiabatic lapse rate*. We shall do this calculation, and see how it compares with actual lapse rates.

As in Section 8.7, the condition for hydrostatic equilibrium is

$$dP = -\rho g dz. \tag{8.8.1}$$

Since we are trying to find a relation between T and z for an adiabatic atmosphere (i.e. one in which P/ρ^γ doesn't vary with height), we need to find the adiabatic relations between P and T and between ρ and T.

These are easily found from the adiabatic relation between P and ρ:

$$P = c\rho^\gamma \tag{8.8.2}$$

and the ideal gas equation of state:

$$P = \frac{\rho RT}{\mu}. \tag{8.8.3}$$

Eliminate P:

$$\rho = \left(\frac{RT}{c\mu}\right)^{1/(\gamma-1)}. \tag{8.8.4}$$

Eliminate ρ:

$$P = \frac{R^{\gamma/(\gamma-1)}}{\mu^{\gamma/(\gamma-1)}c^{1/(\gamma-1)}}T^{\gamma/(\gamma-1)}, \tag{8.8.5}$$

from which

$$dP = \frac{\gamma}{\gamma-1}\frac{R^{\gamma/(\gamma-1)}}{\mu^{\gamma/(\gamma-1)}c^{1/(\gamma-1)}}T^{1/(\gamma-1)}dT. \tag{8.8.6}$$

Substitute equations (8.8.4) and (8.8.6) into equation (8.8.1), to obtain, after a little algebra, the following equation for the adiabatic lapse rate:

$$-\frac{dT}{dz} = \left(1-\frac{1}{\gamma}\right)\frac{g\mu}{R}. \tag{8.8.7}$$

This is independent of temperature.

If you take the mean molar mass for air to be 28.8 kg kmole^{-1}, and g to be 9.8 m s^{-2} for temperate latitudes, you get for the adiabatic lapse rate for dry air −9.7 K km^{-1}. The presence of water vapour in humid air reduces the mean value of μ (and hence the adiabatic lapse rate), and actual lapse rates are usually rather less than the calculated adiabatic lapse rates even for humid air. (The presence of water vapour also increases slightly the value of γ. This would result in a slightly larger lapse rate, but the effect is not as great as the reduction in lapse rate caused by the larger value of μ. Try some numbers to convince yourself of this.) The International Civil Aviation Organization Standard Atmosphere takes the lapse rate in the troposphere (first 11 km) to be −6.3 K km^{-1}. What happens if the actual lapse rate is faster than the adiabatic lapse rate? If you imagine a lump of air to be moved adiabatically to a higher level, its pressure and density will change so that P/ρ^γ is constant, and it will then find itself in a region where its new density is less that the new ambient density. Consequently, it will continue to rise, and the atmosphere will be convectively unstable, and a storm will ensue. The atmosphere is stable as long as the actual lapse rate is less than the adiabatic lapse rate (which is reduced in humid air) is unstable if the actual lapse rate is greater than the adiabatic lapse rate.

8.9: Numerical Values of Specific and Molar Heat Capacities

The following table is not intended as a definitive, authoritative table of precise heat capacities. It is intended just to give a rough idea of the orders of magnitude and the relative magnitudes for a few substances.

For gases, the heat capacities tabulated are at *constant pressure*. For solids and liquids the difference between C_p and C_v is much smaller than for gases, because of the much smaller coefficient of expansion. Notice that the molar heat capacities for gases, when expressed in terms of R, are about what are expected from the theoretical considerations in this chapter. Notice the relatively large molar heat capacities of organic liquids (the molecules can rotate and can vibrate in many modes), and that, the more complex the molecule, the larger its molar heat capacity. Notice, however, that, because water has a low molecular weight (molar mass), water has the largest *specific* heat capacity of any common liquid or solid. (The specific heat capacities of gaseous H_2 and He are, unsurprisingly, larger still. A kilogram of hydrogen is an enormous number of molecules, so it takes a lot of heat to warm them all up.) We have not studied the theory of the heat capacities of solids in this chapter, but, when you do so in a course on solid state physics or on statistical mechanics, you will understand that the expected molar heat capacity of metals would be about $3R$, which is approximately what is shown for the three metals in this table.

		Specific Heat Capacity at Constant Pressure		Molar Heat Capacity at Constant Pressure	
		cal g^{-1} $C^{o\ -1}$	J kg^{-1} K^{-1}	J $kmole^{-1}$ K^{-1}	In units of R
Helium	(g)	1.25	5250	21000	2.53 R
Argon	(g)	0.13	526	21000	2.53 R
H_2	(g)	3.44	14400	28800	3.46 R
O_2	(g)	0.22	919	29400	3.54 R
N_2	(g)	0.25	1040	29100	3.50 R
CO_2	(g)	0.20	843	37100	4.46R
H_2O	(g)	1	4184	75300	9.1 R
C_2H_5OH	(l)	0.58	2430	112000	13.5 R
CCl_4	(l)	0.20	852	131000	15.8 R
C_6H_6	(l)	0.42	1740	136000	16.4 R
Al	(s)	0.22	941	25400	3.1 R
Cu	(s)	0.092	384	24400	2.9 R
Fe	(s)	0.11	450	25100	3.0 R

8.10: Heat Capacities of Solids

I do not deal a great deal with solid state physics in these notes, particularly in this chapter, which has been concerned mostly with gases. But the inclusion of the heat capacities of three metals in the above table provides an opportunity for a brief mention of the heat capacities of metals and of other crystalline solids. In a simple model of a crystalline solid, the solid can be thought of as a regular lattice of atoms held in position near their neighbors by springs, and the atoms have three degrees of vibrational freedom – in the *x*, *y* and *z* directions. For each of these vibrational modes there are two squared terms (of the form $\frac{1}{2}mv^2$ and $\frac{1}{2}I\omega^2$) that contribute to the internal energy. The internal energy associated with each of these six terms is $\frac{1}{2}RT$ per mole, which comes to 3*RT* per mole, and thus you would expect the molar heat capacity to be about 3*R* – and you can see from the above table that this is indeed the case. Indeed at room temperature, most metals and simple crystalline solids have a molar heat capacity of about 3*R*. (This is sometimes referred to as "Dulong and Petit's Rule".) At low temperatures, however, the molar heat falls below this value, and eventually approaches zero at 0 K. At very low temperatures, the molar heat capacity varies roughly as the cube of the temperature. As room temperatures are reached, the molar heat capacity asymptotically approaches the "classical" value of 3*R*.

The run of molar heat capacity with temperature at low temperatures looks a little like figure VIII.5 for magnesium and figure VIII.6 for silver bromide. It will be seen that these two curves are the same shape except for a different scale along the temperature axis – and the same is true for most metals and simple crystalline solids. Indeed we can assign to each solid a characteristic temperature, known as the **Debye temperature**, θ_D, and then, if we express temperature not in kelvin but in units of the Debye temperature for the particular solid, then the curves are indeed the same shape. In other words, the molar heat capacity of all solids (or at least all solids that behave like this!) is the same function of T/θ_D. I show this function as figure VIII.7.

The theory of the heat capacities of solids was investigated by Einstein and by Debye. (Peter Debye – Dutch-American physicist/chemist. Nobel Chemistry prize 1936.) The Debye temperature is related to the vibrational frequency of the atoms in their crystalline lattice. Diamond is a very hard substance, with very strong interatomic bonds. Consequently the vibrational frequencies are very high, and the Debye temperature for diamond is correspondingly high: θ_D = 1860 K. As a result of this the heat capacity rises very slowly with increasing temperature, and at room temperature is well below the "classical" value of 3*R*. Most other solids have weaker bonds and far lower Debye temperatures, and consequently their molar heat capacities have almost reached the classical Dulong-Petit value of 3*R* at room temperature. Here are a few Debye temperatures:

Elements	Debye temperature
Potassium	100K
Silver bromide	145
Silver	215
Magnesium	290
Copper	315
Iron	420

If it seems that the harder the solid the higher the Debye temperature and the slower the solid is to reach its classical C_V of 3*R*, this is not coincidence.

I do not derive Debye's theoretical formula here – it is something to look forward to in courses on solid state physics or statistical mechanics, but, for interest, the formula (which I used for calculating figures VIII.5-7) is

$$C_V = 9T^3 \int_0^{1/T} \frac{x^4 e^x}{(e^x - 1)^2} dx. \tag{8.10.1}$$

In this equation C_V is in units of *R*, and *T* is in units of the Debye temperature.

FIGURE VIII.5

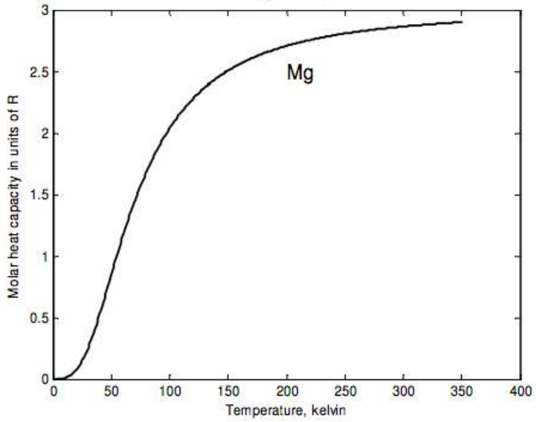


FIGURE VIII.6

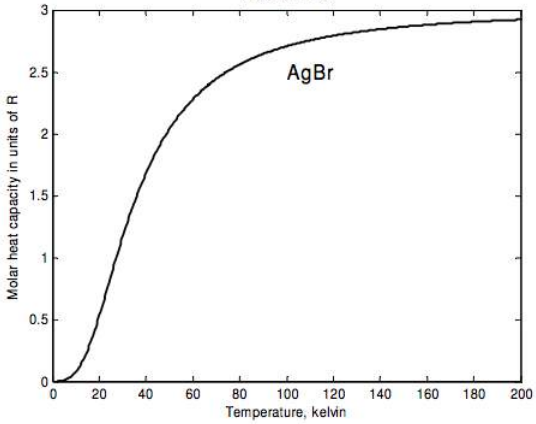
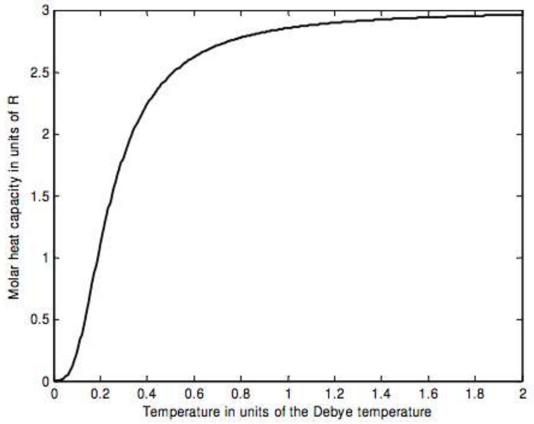


FIGURE VIII.7



In case you are wondering what the symbol “*x*” stands for in equation 8.9.1, it is merely a dummy variable, for the integral in that expression is a function not of *x* but of *T*, the upper limit of the integral.

If you try to reproduce figure VIII.7 yourself by evaluating equation 8.9.1 for a number of different temperatures, you will soon find that it is a good deal more laborious than may at first be evident.

In my first attempt at doing it, for each of the 400 values of *T* that I used for plotting Figure VIII.7, I used a 1000 point Simpson’s Rule integration. Thus I evaluated the integrand 400,000 times, and it took the computer almost half a second. Later, I found that Gaussian quadrature was much, much more efficient, requiring the calculation of the integrand at only a very few points.

However, J. Viswanathan of Chennai, India, has since shown me an even better method than the Gaussian quadrature.

He uses the theorem

$$\frac{d}{dx}\int_0^{g(x)} f(y)dy = f(g(x))g'(x)$$

This was a new one on me, but it is very easy to derive and looks almost obvious in hindsight. Applied to our problem, that is, applied to our equation

$$C_V = 9T^3 \int_0^{1/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx, \tag{8.10.2}$$

it becomes, after a modest amount of work:

$$\frac{dC_V}{dT} = \frac{3C_V}{T} - 9Tf(1/T), \tag{8.10.3}$$

where

$$f(x) = \frac{x^4 e^x}{\left(e^x - 1\right)^2}. \tag{8.10.4}$$

He evaluates C_V at T = 2, using a direct numerical integration of equation 8.9.1 - but this is the *only* time that he does this! The answer is 2.9628. Then he moves down by dT at each step and calculates the corresponding dC_V by using a fourth order Runge-Kutta integration on the differential equation 8.9.3. The three methods agree very well, but the Simpson's Rule method was by far the most laborious.

Debye's theory was published in 1912, and they certainly didn't have electronic computers, or even electronic hand calculators, in those days. In the 1950s most scientists were using hand-operated mechanical calculators, with electrically-driven mechanical calculators beginning to come into use towards the end of that decade. I suspect that in 1912 not even hand-operated mechanical calculators were available, and calculations would have been done using pencil and paper and logarithm and other tables. One must think of the physical insight and mathematical competence needed to develop the theory of the heat capacity in the first place, and then the enormous effort needed to calculate the resulting equations.

CHAPTER OVERVIEW

9: Enthalpy

9.1: Enthalpy

Enthalpy is sometimes known as "heat content", but "enthalpy" is an interesting and unusual word, so most people like to use it. Etymologically, the word "entropy" is derived from the Greek, meaning "turning" (I'm not sure why) and "enthalpy" is derived from the Greek meaning "warming". As for pronunciation, ENtropy is usually stressed on its first syllable, while enTHALpy is usually stressed on the second. Again, I am not sure why.

Definition: *Enthalpy* H is defined as

$$H = U + PV. \tag{9.1.1}$$

You now know the etymology of enthalpy, you know how to spell it, you know its pronunciation, and you even know its definition. But you don't yet know what it *means*. You cannot determine the internal energy of a system to start with (you can only determine an *increase* in it), but what on Earth does it mean to add to the (undetermined) internal energy the product of the pressure and the volume?

Well, let us see how the enthalpy changes if we change the pressure and volume (and hence the internal energy) of a system. We'll just differentiate Equation 9.1.1.

$$dH = dU + PdV + VdP \tag{9.1.2}$$

But $dU = TdS - PdV$, and so the first law becomes

$$dH = TdS + VdP \tag{9.1.3}$$

This helps us to see a little more the meaning of enthalpy. In particular, for a reversible process, $TdS = dQ$, and so Equations 7.3.2 and 9.1.3 become, respectively,

$$dU = dQ - PdV \tag{9.1.4}$$

and

$$dH = dQ + VdP \tag{9.1.5}$$

Thus we can say:

> *The increase of the internal energy of a system is equal to the heat added to it in an isochoric process,*

and

> *The increase of the enthalpy of a system is equal to the heat added to it in an isobaric process.*

Experiments carried out in open beakers on a laboratory bench are isobaric. Thus the heat generated during a chemical reaction in an open beaker represents the generation of enthalpy. You will notice that chemists use the symbol *H* for heat of reaction, and they are well aware that this means enthalpy. If the reaction were carried out, however, in an autoclave (also known as a pressure cooker), the heat generated represents the generation of internal energy.

I hope that this now gives some meaning to the concept of enthalpy.

Internal energy *U* and enthalpy *H* are both functions of state. From Equation 7.3.2 ($dU = TdS - PdV$) we immediately see the relations

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{9.1.6}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_s = -P. \tag{9.1.7}$$

From Equation 9.1.3 ($dH = TdS + VdP$) we immediately see the relations

$$\left(\frac{\partial H}{\partial S}\right)_P = T \tag{9.1.8}$$

and

$$\left(\frac{\partial H}{\partial P}\right)_S = V. \tag{9.1.9}$$

Also from Equation 7.3.2 ($dU = TdS - PdV$) we obtain (since dU is an exact differential)

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_V, \tag{9.1.10}$$

and from Equation 9.1.3 ($dH = TdS + VdP$) we obtain (since dH is an exact differential)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \tag{9.1.11}$$

Equations 9.1.10 and 9.1.11 are two of *Maxwell's Thermodynamic Relations*. (There are two more to come, in a later chapter.)

We also note that, while the heat capacity at constant volume is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \tag{9.1.12}$$

similarly the heat capacity at constant pressure is

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P. \tag{9.1.13}$$

9.2: Change of State

According to my dictionary, the word "latent" means "present or existing and capable of development but not manifest".

In a liquid at its freezing point there is present or existing some heat, which is capable of development but is not manifest. That is, the liquid secretly holds some latent heat. When the liquid freezes, it gives up this latent heat to its surroundings. The heat is now manifest.

Definition: The *latent heat of freezing* of a quantity of liquid at its freezing point is the heat given up to its surroundings when it freezes. Its SI unit is the joule.

Likewise, we define the *specific latent heat* and the *molar latent heat* of a liquid at its freezing point as the heat given up when unit mass, or a molar amount, respectively, freezes. The SI units are J kg^{-1} and J kilomole^{-1} respectively.

> A distressingly large number of people use the words "latent heat" when they mean "specific latent heat". Thus, when you read or hear the words "latent heat" you have to be on guard to decide whether this is really what is meant, or whether "specific latent heat" is intended.

The latent heat of *fusion* of a solid body at its melting point is the heat required to melt it. This is just equal to the heat given up when the liquid freezes, so that, numerically, the latent heats of freezing and of fusion (melting) are the same – though somehow the word "latent" seems less appropriate for freezing, because you are supplying heat to the solid, rather than seeing latent heat being released by a liquid. If you prefer you could refer to the "latent heat" of fusion simply as the "heat of fusion" – or as the “enthalpy of fusion”.

Likewise we have a latent heat of condensation of a vapour at its condensation point, and the latent heat of vaporization of a liquid at its boiling point. These are equal in magnitude. We can also define the specific and molar latent heats of condensation and vaporization. The term latent heat of transformation will do to cover all four processes. The symbol L (with appropriate subscripts if need be) can be used for any of the latent heats of transformation.

The specific latent heat of fusion of ice at atmospheric pressure is about 3.36 × 105 J kg^{-1} or about 80 cal g^{-1}.

The specific latent heat of vaporization of water at atmospheric pressure is about 2.27 × 106 J kg^{-1} or about 540 cal g^{-1}.

Example 9.2.1

70 g of ice at 0 °C are mixed with 150 g of water at 100 °C. What is the final temperature? (I make it 43° C.)

Solution

We'll reluctantly, for once, work in calories and grams, and of course the specific heat capacity of water is about 1 calorie per gram per Celsius degree. The heat required to melt the 70 g of ice, and then to raise its temperature from 0 °C to *t* °C is 70 × 80 + 70*t* calories. This heat is supplied by the hot water, which cools from 100 °C to *t* °C, is 150 % (100 − t) calories. Equating the two produces *t* = 43 °C.

Example 9.2.1

Suppose you apply 2.27 × 10^6 J of energy to a kilogram of water, but, instead of using that energy to vaporize the water, you use it to raise the water from the ground. How high above the ground could you raise it with this energy? It may surprise you – it certainly surprised me! If you were to use the energy, not to vaporize the water, and not to raise it above the ground, but to throw it, how fast, in miles per hour, could you throw it?

For many liquids there is a very rough correlation between molar latent heat of vaporization and boiling point at atmospheric pressure, the ratio L/T usually being in the range 70,000 to 100,000 J kmole^{-1} K^{-1}.

One last point before proceeding. Generally it is only crystalline solids (including metals) that have a rather definite melting point. Amorphous substances such as plastics and glass generally change from solid to liquid over a rather large range of temperature. Indeed is not obvious when to cease calling such a substance a solid and to start calling it a liquid. Some writers would describe glass as a “liquid” even when it has all the obvious appearances of a solid. See also Section 6.4 for a further discussion of this. Mixtures, alloys and solutions, too, do not have such a definite melting point as a crystalline solid, and a salt solution does not have as definite a boiling point (at a given pressure) as a pure liquid does. Thus a salt solution in water at one atmosphere pressure boils at a little higher temperature than 100 °C. When some of the water boils off, the remaining solution is a little more concentrated, and so the boiling point becomes a little higher, and so on.

9.3: Latent Heat and Enthalpy

Consider a liquid of volume V_1 at its boiling point. Suppose a quantity of heat L is supplied, sufficient to vaporize the liquid. The new volume (of what is now vapour) is V_2. If the vapour has expanded against a constant pressure P (e.g. the pressure of the atmosphere), the work done by it is $P(V_2 - V_1)$. The increase in the internal energy of the system is the heat supplied to the system minus the work done by it (this is the engineer's version of the first law of thermodynamics). That is, $U_2 - U_1 = L - P(V_2 - V_1)$, and so

$$H_2 - H_1 = L. \tag{9.3.1}$$

So, during a change of state at constant pressure the increase or decrease of enthalpy is equal to the latent heat of transformation. This, of course, is just a simple example of our earlier statement, in Section 9.1, that the increase of enthalpy of a system is equal to the heat supplied to it in an isobaric process.

CHAPTER OVERVIEW

10: The Joule and Joule-Thomson Experiments

10.1: Introduction

Equation 8.4.3, $TV^{\gamma-1} = \text{constant}$, tells us how to calculate the drop in temperature if a gas expands adiabatically and reversibly; it is expanding against an external pressure (e.g., a piston), and, in pushing the piston back, the molecules are doing external work and are losing kinetic energy. What happens, however, if a gas expands into a vacuum? Suppose that the gas is held inside a cylinder not by a metal piston but by a thin membrane, and the membrane breaks, so that the molecules rush out into empty space. This is obviously an *irreversible* expansion; it is most unlikely that all of the molecules will ever find their way back to the cylinder. The molecules are doing no external work. If the gas is an ideal gas, there are no intermolecular forces, so the gas does no internal work. There is nothing to slow down the molecules in their headlong escape from the cylinder. The temperature will remain unaltered by the expansion. On the other hand, if the gas is not an ideal gas, there will be van der Waals attractive forces between the molecules, so the molecules will slow down slightly when the gas expands and there will be a small drop in temperature. But we also recall, from the van der Waals model, that at close intermolecular distances, the forces between the molecules are predominantly repulsive Coulomb forces, so it is also possible that, if the gas starts out very dense and it expands irreversibly as we have described, it may initially become slightly warmer as the repulsive Coulomb forces push the molecules apart and speed them on their way.

The Joule and Joule-Thomson experiments are concerned with these scenari.

10.2: The Joule Experiment

In Joule's original experiment, there was a cylinder filled with gas at high pressure connected via a stopcock to a second cylinder with gas at a low pressure – sufficiently low that, for the purpose of understanding the experiment, we shall assume the second cylinder to be entirely empty. The two cylinders were immersed in a water bath, and the stopcock was opened so that gas from the high pressure cylinder flowed into the evacuated cylinder. No heat was supplied to or lost from the system, nor did the gas do any work, so the *internal energy* was constant during the expansion. Joule found no temperature fall as a result of the expansion. This, as we have argued in Section 10.1, is exactly what we would expect for an ideal gas; that is, for an ideal gas, the temperature is independent of the volume if the internal energy is constant. That is, for an ideal gas,

$$\underbrace{\left(\frac{\partial T}{\partial V}\right)_U = 0.}_{\text{Ideal Gas}} \tag{10.2.1}$$

For a real gas, however, we would expect a small drop in temperature, and $\left(\frac{\partial T}{\partial V}\right)_U$, which is called the **Joule coefficient**, is not zero. The heat capacity of the water bath and the cylinders in Joule's original experiment, however, was too large for him to detect any fall of temperature even with a real gas. More sensitive experiments found that almost all gases cool during a Joule expansion at all temperatures investigated; the exceptions are helium, at temperatures above about 40 K, and hydrogen, at temperatures above about 200 K.

$$\underbrace{\left(\frac{\partial T}{\partial V}\right)_U \neq 0.}_{\text{Real Gas}} \tag{10.2.2}$$

We should be able to derive an expression for the Joule coefficient, given the equation of state, and we should also be able to show that, if the equation of state is the equation of state for an ideal gas, the Joule coefficient is zero.

Internal energy and enthalpy are both functions of state; that is, they are functions of *P*, *V* and *T*. However, any particular substance cannot exist at any arbitrary point in *PVT*-space, but is constrained to be on the two-dimensional surface represented by its *equation of state*. Figures VI.7, 8 and 9 of Chapter 6 represent an example of such a surface. In other words, *P*, *V* and *T* cannot be varied independently; they are connected by an equation of the form $f(P,V,T)=0$. Thus internal energy and enthalpy can be described by a function of just two of the state variables *P*, *V* and *T*. In the experiment we are discussing, we are interested in how temperature varies with volume in an experiment in which the internal energy is constant. We shall therefore choose *U* as our state function and *V* and *T* as our independent state variables. That is, we shall write $U=U(V,T)$, so that

$$\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial U}\right)_T = -1. \tag{10.2.3}$$

Our aim, of course, is to find an expression for the Joule coefficient $\left(\frac{\partial T}{\partial V}\right)_U$, for which I shall be using the symbol η.

The second of these partial derivatives is C_V, and therefore

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T. \tag{10.2.4}$$

Now

$$dU = TdS - PdV. \tag{10.2.5}$$

That is,

$$dS = \frac{1}{T}[dU + PdV] \tag{10.2.6}$$

$$= \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + PdV\right]. \tag{10.2.7}$$

$$= \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT. \tag{10.2.8}$$

But we also have

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT. \tag{10.2.9}$$

Therefore

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \tag{10.2.10}$$

and

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V. \tag{10.2.11}$$

The mixed second derivatives are

$$\frac{\partial^2 S}{\partial T \partial V} = -\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + \frac{1}{T}\left[\frac{\partial^2 U}{\partial T \partial V} + \left(\frac{\partial P}{\partial T}\right)_V\right] \tag{10.2.12}$$

and

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T}. \tag{10.2.13}$$

But entropy is a function of state and dS is an exact differential, so the mixed second derivatives are equal. Whence, after simplification:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{10.2.14}$$

Hence, returning to Equation 10.2.4, we obtain, for the Joule coefficient,

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U \tag{10.2.15}$$

$$= \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right]. \tag{10.2.16}$$

Exercise 10.2.1

Show that, for an ideal gas, the Joule coefficient is zero.

Example 10.2.1

Show that, for a van der Waals gas, the Joule coefficient is

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{a}{C_V V^2}.$$

Hence, for a finite volume change,

$$T_2 = T_1 - \frac{a}{C_V}\left(\frac{1}{V_1} - \frac{1}{V_2}\right).$$

Solution

For example, the volume of a kmole of CO_2 at a temperature of 20 °C (293.15 K) and a pressure of 1 atm (1.013 × 105 Pa) is $V_1 = RT/P = 24.06\ \text{m}^3$. (That's a lot of cubic metres – but then 44 kg of CO_2 is a lot of carbon dioxide.). If its volume were doubled to 48.12 m3 in an irreversible Joule-type expansion, what would be its new temperature? From Chapter 6, we find a = 3.7 × 105 Pa m^6 kmole^{-1}, and from Chapter 8 we find that C_P = 37100 J kmole^{-1} K^{-1} and therefore let's take C_V = 28786 J kmole^{-1} K^{-1}, and so we obtain T_2 = 292.88 K = 19.73 °C. This cooling is a result not of the gas doing external work as in a reversible adiabatic expansion, but of doing work against the internal van der Waals forces between the molecules. What would be the temperature drop in a reversible adiabatic expansion? The new temperature would be given by $T_2 = \left(\frac{V_1}{V_2}\right)^{\gamma-1} T_1$. Let's take $\gamma = 37100 \div 28786 = 1.29$. Then $T_2 = (1/2)^{0.29} \times 293.15 = 239.77$ K = −33.38 °C at which temperature it would easily have sublimated into solid CO_2. In this calculation, I used $C_P - C_V = R$ and $TV^{\gamma-1}$ = constant, which are valid only for an ideal gas. We'll shortly derive a more general expression for $C_P - C_V$, but the correction for nonideality will obviously be quite small.

10.3: The Joule-Thomson Experiment

The experiment is also known as the Joule-Kelvin experiment. William Thomson was created Lord Kelvin. The experiment is also known as the porous plug experiment.

In the Joule-Thomson experiment a constant flow of gas was maintained along a tube which was divided into two compartments separated by a porous plug, such that the pressure and molar volume on the upstream side were P_1, V_1, and the pressure and molar volume on the downstream side were P_2, V_2. Under such circumstances the **net** work done **on** a mole of gas in passing from one compartment to the other is $P_1V_1 - P_2V_2$. (Imagine, for example, that a piston pushes a mole of gas towards the plug from the upstream side, through a distance x1 ; if A is the crosssectional area of the tube, the work done **on** the gas is $P_1Ax_1 = P_1V_1$. Imagine also that the gas on the downstream side pushes a piston away from the plug through a distance x_2. The work done by the gas is $P_2Ax_2 = P_2V_2$. Therefore the net external work done **on** the gas is $P_1V_1 - P_2V_2$.) If no heat is supplied to or lost from the system, the increase in internal energy of this gas is just equal to this work done on it:

$$U_2 - U_1 = P_1V_1 - P_2V_2,$$

or

$$U_1 + P_1V_1 = U_2 + P_2V_2. \tag{10.3.1}$$

That is, there is no change in enthalpy. Therefore, we want to find $\left(\frac{\partial T}{\partial P}\right)_H$, which is the *Joule-Thomson coefficient*, for which I shall be using the symbol μ.

In the experiment we are discussing, we are interested in how temperature varies with pressure in an experiment in which the enthalpy is constant. We shall therefore choose H as our state function and P and T as our independent state variables. That is we shall write $H = H(P,T)$, so that

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial P}{\partial H}\right)_T = -1. \tag{10.3.2}$$

The second of these partial derivatives is C_P, and therefore

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T. \tag{10.3.3}$$

Now

$$dH = TdS + VdP. \tag{10.3.4}$$

That is,

$$dS = \frac{1}{T}[dH - VdP] = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT - VdP\right]. \tag{10.3.5}$$

$$dS = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT. \tag{10.3.6}$$

But we also have

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT. \tag{10.3.7}$$

Therefore

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \tag{10.3.8}$$

and

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p. \tag{10.3.9}$$

The mixed second derivatives are

$$\frac{\partial^2 S}{\partial T \partial P} = -\frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] + \frac{1}{T}\left[\frac{\partial^2 H}{\partial T \partial P} - \left(\frac{\partial V}{\partial T}\right)_P\right] \tag{10.3.10}$$

and

$$\frac{\partial^2 S}{\partial P \partial T} = \frac{1}{T}\frac{\partial^2 H}{\partial P \partial T}. \tag{10.3.11}$$

But entropy is a function of state and dS is an exact differential, so the mixed second derivatives are equal. Whence, after simplification:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P. \tag{10.3.12}$$

Hence, returning to equation 10.3.3, we obtain, for the Joule-Thomson coefficient,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]. \tag{10.3.13}$$

Trivial Exercise: Show that, for an ideal gas, the Joule-Thomson coefficient is zero, and also that, for an ideal gas,

$$\left(\frac{\partial H}{\partial P}\right)_T = 0. \tag{10.3.14}$$

This is analogous to equation 8.1.4 for an ideal gas, namely $\left(\frac{\partial U}{\partial V}\right)_T = 0$.

Exercise. Show that, for a van der Waals gas, the Joule-Thomson coefficient is

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{V}{C_p}\cdot\frac{\left(RTV^2b - 2a(V-b)^2\right)}{RTV^3 - 2a(V-b)^2}. \tag{10.3.15}$$

(Verify the dimensions of this expression.) Hint: It is difficult to calculate $(\partial V/\partial T)_P$ directly, because it is difficult to express V explicitly as a function of P and T. It is not actually impossible to do it algebraically, because van der Waals' equation is a cubic equation in V, and a cubic equation does have an algebraic solution. It is easier, however, to calculate $(\partial V/\partial T)_P$ from $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V / \left(\frac{\partial P}{\partial V}\right)_T$, or from $\left(\frac{\partial V}{\partial T}\right)_P = 1/\left(\frac{\partial T}{\partial V}\right)_P$.

Note also that the Joule-Thomson coefficient may be negative or positive; i.e., it may result in cooling or heating. It will result in heating if you start above a certain temperature called the *inversion temperature*, and cooling if you start below the inversion temperature. The Joule-Thomson effect is used in the *Linde method* for cooling and ultimately liquefying gases. For most gases, the inversion temperature is higher than room temperature, so that cooling starts immediately. But for hydrogen, the inversion temperature is about −80 $^{\circ}$C, and hydrogen must be cooled below this temperature before the Joule-Thomson effect can be used to cool it further and to liquefy it. You can see from equation 10.3.14 that the inversion temperature for a van der Waals gas is equal to $\frac{2a(V-b)^2}{RV^2b} \approx \frac{2a}{Rb}$. Here V is the molar volume.

Summary:

Joule coefficient

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right] \tag{10.3.16}$$

Joule-Thomson coefficient

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]. \tag{10.3.17}$$

10.4: CP Minus CV

In Section 8.1 we pointed out that the heat capacity at constant pressure must be greater than the heat capacity at constant volume. We also showed that, for an ideal gas, $C_P = C_V + R$, where these refer to the molar heat capacities. We said that in Chapter 10 we would try and develop a more general expression for $C_P - C_V$, which was applicable in general and not only for an ideal gas. Some of the relations that we developed in Sections 10.2 and 10.3 give us the opportunity to try to do that now.

Let us consider an isobaric process and express the internal energy U as a function of V and T. (As we have pointed out, P, V and T are not independent variables because they are connected through the equation of state, so we may choose any two of them as independent variables.) Then, if the volume and temperature increase by infinitesimal amounts, the corresponding increase in the internal energy is given by

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT. \tag{10.4.1}$$

I.e.,

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT \tag{10.4.2}$$

Consider how the first law:

$$dU = dQ + dW. \tag{10.4.3}$$

In an isobaric process, $dQ = C_p dT$, and in a reversible process, $dW = -PdV$.

Therefore

$$C_P dT - PdV = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT \tag{10.4.4}$$

Divide by dT, recalling that we are considering an isobaric process:

$$C_P - P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + C_V. \tag{10.4.5}$$

Hence

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P. \tag{10.4.6}$$

This is a useful general expression, as long as we know or can determine $(\partial U/\partial V)_T$. (Note that the extensive quantities can be total, specific or molar.)

Let us just test this by applying it to an ideal gas to see if it produces the result that it ought to produce. For an ideal gas, the internal energy at a given temperature is independent of the volume. This is because in an ideal gas there are no intermolecular forces, so that, as the volume increases and the intermolecular distances increase, there is no change in potential energy; and, if the temperature is constant, so is the kinetic energy. Thus, for an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$. The volume of a mole of ideal gas is $V = RT/P$, so that $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$.

Therefore

$$C_P - C_V = P \times \frac{R}{P} = R, \tag{10.4.7}$$

and all is well.

For any substance other than an ideal gas, we shall need to know $\left(\frac{\partial U}{\partial V}\right)_T$ before we can make use of equation 10.4.6. But equation 10.2.12, which we developed in Section 10.2 while analysing the Joule effect, enables us to do just this:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{10.4.8}$$

On combining this with equation 10.4.6, we obtain

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{10.4.9}$$

Depending on the equation of state, it may or may not be easy to evaluate these partial derivatives. For example, for the van der Waals equation of state (which is a cubic equation in V), it is not easy to evaluate $(\partial V/\partial T)_P$ directly, but one can then make use of $(\partial V/\partial T)_P$ = $(\partial V/\partial T)_P$ or of $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$ in order to get $C_P - C_V$ in terms of easily evaluable partial derivatives. For example

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right) / \left(\frac{\partial T}{\partial V}\right)_P \text{ or } -T\left(\frac{\partial P}{\partial T}\right)_v^2 / \left(\frac{\partial P}{\partial V}\right)_T \tag{10.4.10}$$

or several other variants.

Any of equations 10.4.8 or 10.4.9 can be used to calculate $C_P - C_V$; it just depends on which of the derivatives, for a particular equation of state, are easiest to calculate.

The reader will easily be able to show that, for a mole of an ideal gas, this becomes just $C_P - C_V = R$. A little more algebra will be needed to show that, for a mole of a van der Waals gas,

$$C_P - C_V = \frac{R}{1-2a(V-b)^2/(RTV^3)} = R\cdot\frac{P+a/V^2}{P-a/V^2+2ab/V^3} \approx R\cdot\frac{(RT)^2+aP}{(RT)^2-aP}. \tag{10.4.11}$$

In the above analysis, we considered an isobaric process and we chose the internal energy as our function of state and we started by calculating the increment in U corresponding to increments dV and dT in the volume and temperature. It is tempting now to go through the same analysis, but this time to consider an isochoric process and to choose the enthalpy as our function of state. We start by calculating the increment in H corresponding to increments dP and dT in the pressure and temperature:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT. \tag{10.4.12}$$

I.e.,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT. \tag{10.4.13}$$

Now

$$H = U + PV, \quad \therefore dH = dU + PdV + VdP = dQ + dW + PdV + VdP. \tag{10.4.14}$$

Provided that we include in dQ any irreversible work that is being done on the system (irreversible work has the same effect, as we have seen, as adding heat), so that $dW = -PdV$, then

$$dH = VdP + dQ = VdP + C_V dT. \tag{10.4.15}$$

On comparison of equations 10.4.11 and 10.4.12 we obtain

$$VdP + C_V dT = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT. \tag{10.4.16}$$

Divide by dT, recalling that we are considering an isochoric process. From this, we obtain an alternative expression for the difference between the heat capacities:

$$C_P - C_V = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V. \tag{10.4.17}$$

This is quite analogous to equation 10.4.6. It is left to the reader to show that, for an ideal gas, this reduces to $C_P - C_V = R$. This will be easy if you recall equation 10.3.14, for an ideal gas: $\left(\frac{\partial H}{\partial P}\right)_T = 0$.

For any substance other than an ideal gas, we shall need to know $\left(\frac{\partial H}{\partial P}\right)_T$ before we can make use of equation 10.4.15. But equation 10.3.12, which we developed in Section 10.3 while analysing the Joule-Thomson effect, enables us to do just this:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P. \tag{10.4.18}$$

On combining this with equation 10.4.15, we obtain again equation 10.4.8. We obtained no new result for $C_P - C_V$ (although we did obtain the important result 10.4.16 for an ideal gas), but it is satisfying and instructive to have obtained the same result via internal energy and via enthalpy.

After this, we can hardly resist the temptation to see what happens if we treat P and V as independent variables. Thus, if $U = U(P, V)$, then increases of dP and dV in the pressure and volume result in an increase dU of the internal energy given by

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV. \tag{10.4.19}$$

But we already know (equation 10.4.1), by choosing the independent variables to be T and V, that

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT. \tag{10.4.20}$$

And from the equation of state $T = T(P, V)$, we derive that

$$dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV. \tag{10.4.21}$$

By elimination of dT from equations 10.4.1 and 10.4.18 we obtain

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial U}{\partial V}\right)_T dV. \tag{10.4.22}$$

On comparison of equations 10.4.17 and 10.4.19 we deduce the following relations, which are occasionally useful:

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V, \tag{10.4.23}$$

(which I hope we already knew!)

and

$$\left(\frac{\partial U}{\partial V}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T. \tag{10.4.24}$$

The first of these is, of course, trivial, and does not require this lengthy derivation. The second is a worthwhile relation, which we may occasionally find useful.

Summary:

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right] \left(\frac{\partial P}{\partial T}\right)_V \tag{10.4.25}$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \text{ and variants.} \tag{10.4.26}$$

10.5: Blackbody Radiation

Before we forget all the equations in this chapter, let's use equation 10.2.12 (which we have already used twice – once in the derivation of the Joule-Thomson coefficient and once in the derivation of $C_P - C_V$) in a totally different application:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{10.5.1}$$

This is a very general thermodynamical relation, and is by no means restricted to Joule's experiment. Let us apply it to electromagnetic radiation (rather than molecules) in an enclosure.

You may already have studied the theory of radiation in a cavity and the closely-related theory of blackbody radiation. You will know that classical electromagnetic theory failed to explain the observed characteristics of blackbody radiation, and that it was not explained fully until the advent of quantum theory. In the middle of the nineteenth century Kirchhoff argued theoretically that the energy density inside a cavity was independent of the nature of the walls of the cavity and depended only on the temperature and the wavelength. Stefan had shown experimentally that the radiation density inside a cavity integrated over all wavelengths was proportional to the fourth power of the temperature. Later on, Lummer and Pringsheim did some detailed measurements which showed how the radiation density per until wavelength varied with wavelength and temperature. It was shown by Rayleigh and Jeans that classical electromagnetic theory failed badly at short wavelengths to explain the observed distribution of the cavity radiation with wavelength. In 1900 Planck, without quite knowing why, showed that, if he regarded radiation as being made up of quanta of energy hv, the energy density per unit volume per unit wavelength interval would be expected to vary as $u_\lambda = \frac{C_1}{\lambda^5\left(e^{C_2/\lambda T}-1\right)}$ which agreed very well with the experimental data of Lummer and Pringsheim. You also may know that if you integrate this expression over all wavelengths (not particularly easy), you find that $\int u_\lambda d\lambda$ is proportional to T^4, thus also agreeing with the observations of Stefan.

However, although quantum theory was necessary to explain the Lummer-Pringsheim measurements of how u_λ varies with temperature, Boltzmann used classical thermodynamical theory to explain Stefan's T^4 law almost immediately after Stefan had announced his results, and long before the advent of quantum theory. The theory of radiation tells us that the radiation energy per unit volume u depends only on the temperature (this is Kirchhoff's radiation law) and that the radiation pressure P is related to the energy per unit volume by $P = \frac{1}{3}u$. The derivation of this is very similar to the expression that we derived for the pressure of molecules in a gas. For this situation, equation 10.2.12 becomes

$$u = \frac{1}{3}T\frac{du}{dT} - \frac{u}{3}, \tag{10.5.2}$$

or

$$4u = T\frac{du}{dT}. \tag{10.5.3}$$

Integration of this (do it!) shows that u ∝ T^4, without any need for quantum theory.

This is often written as u ∝ aT^4, but beware, here a is not what it generally known as "Stefan's constant". See Chapters 1 and 2 (especially Section 1.17) of my Stellar Atmospheres notes for more on this. Stefan's Law generally refers to the exitance of a black body surface, $M = \sigma T^4$, whereas here we are referring to the energy density of radiation in a cavity. The relation between a and Stefan's constant σ is $a = 4\sigma/c$.

Now suppose that you had some radiation at temperature T in an enclosure (such as The Universe) of volume V. And suppose that volume were to expand adiabatically, thus diluting the energy density. What would be the new temperature? In what follows, V means the volume (not the "specific" or "molar" volume) of the enclosure. U is the internal energy of the radiation inside it, and u is the radiation energy density, such that $U = uV$, and we shall be making use of $P = \frac{1}{3}u$ and of $u = aT^4$.

If the volume were to increase by dV at pressure P, the work done by the radiation would be $PdV = \frac{1}{3}udV$, and, if we assume that the expansion is adiabatic, this results (by the first law of thermodynamics) in a decrease of the internal energy. We apply the first law: $dU = -PdV$. That is

$$d(uV) = udV + Vdu = -\frac{1}{3}udV. \tag{10.5.4}$$

$$\frac{dV}{V} = -\frac{3}{4}\frac{du}{u}. \tag{10.5.5}$$

Therefore

$$V \propto u^{-3/4} \quad \text{or } u \propto V^{-4/3}. \tag{10.5.6}$$

But u ∝ T^4 and hence

$$VT^3 \text{ is constant,} \tag{10.5.7}$$

or the temperature is inversely proportional to the linear dimensions of the enclosure.

CHAPTER OVERVIEW

11: Heat Engines

Topic hierarchy

11.1: Introduction

In my rarefied, theoretical, academic and unpractical mind, a heat engine consists of a working substance obeying some idealized equation of state such as that for an ideal gas, held inside a cylinder by a piston, and undergoing, in a closed cycle, a series of highly idealized processes, such as reversible adiabatic expansions or isothermal compressions. At various stages of the cycle, the system may be gaining heat from or losing heat to its surroundings; or we may be doing work on the system by compressing it, or the system may be expanding and doing external work.

The *efficiency* η of a heat engine is defined as

$$\eta=\frac{\text{net external work done }\mathbf{by}\text{ the engine during a cycle}}{\text{heat supplied }\mathbf{to}\text{ the engine during a cycle.}}\tag{11.1.1}$$

By “net” external work, I mean the work done **by** the engine during that part of the cycle when it is doing work *minus* the work done **on** the engine during that part of the cycle when work is being done on it. Notice that the word “net” does not appear in the denominator, which refers only **to** the heat supplied to the engine during that part of the cycle when it is gaining heat.

During the compression part of the cycle, the system gives out heat, and only the difference “heat in *minus* heat out” is available to do the external work. Thus efficiency can also be calculated from

$$\eta=\frac{Q_{\text{in}}-Q_{\text{out}}}{Q_{\text{in}}}.\tag{11.1.2}$$

although the definition of *efficiency* remains as equation 11.1.1.

No heat engine is 100% efficient, and we need to ask what is the most efficient heat engine possible, what are the factors that limit its efficiency, and what is the greatest possible efficiency? Obviously things like friction in the moving parts of the engine limit the efficiency, but in my academic mind the engine is built with frictionless bearings and all processes in the cycle of compressions and expansions are reversible.

During a cycle, a heat engine moves in a clockwise closed path in the *PV* plane, and, if the processes are reversible, the area enclosed by this clockwise path is the net external work done **by** the system. It also moves in a clockwise closed path in the *TS* plane, and, if the processes are reversible, the area enclosed by this clockwise path is the net heat supplied to the system. The two are equal, and when the system returns to its original state, there is no change in the internal energy. That is, internal energy is a function of state.

Depending upon the nature of the various processes during the cycle, the cycle may carry various names, such as the Carnot, Stirling, Otto, Diesel or Rankine cycles. Of these, the most important from the theoretical point of view is the Carnot cycle. I do not know whether anyone has ever built a Carnot heat engine. I do know, however, that no one has ever built an engine working between a hot heat source and a cold heat sink that is more efficient than a Carnot engine; for, for a given temperature difference between source and sink, the Carnot engine is the most efficient conceivable. There is another important thing about the Carnot cycle. In Chapter 3, we struggled to understand that most difficult of all the thermodynamic concepts, namely *temperature*, and we wondered if we could define an *absolute* temperature scale that was independent of the properties of any particular substance. Consideration of the Carnot cycle enables us to do just that.

Of real heat engines I know very little. I know that one pedal of my car makes the car go faster and the other makes it go slower – but what is under the hood or bonnet is beyond my ken. Real heat engines may resemble some of the theoretical engines of academia to a greater or lesser extent. Thus a motor car engine may resemble an Otto cycle, or a steam engine may resemble a Rankine cycle, or a real Diesel engine may resemble the theoretical Diesel cycle. Engineering students may wonder whether they need bother with learning about “theoretical” engines that bear little resemblance to the metal and fuel that they have to work with on a practical basis. I cannot answer that, but there is just one thing I *do* know about real engines, and that is that they are subject to and follow all the fundamental laws of thermodynamics that theoretical engines have to follow; and I suspect that the engineer who designed the engine in my car had a pretty thorough knowledge of the fundamental principles of thermodynamics.

11.2: The Carnot Cycle

I referred above to one of the uses of the theoretical concept known as the Carnot cycle, namely that it enables us to define an absolute temperature scale. I suggest that, before you read any further, you re-read Section 3.4 of Chapter 3.

Pause while you re-read Section 3.4

As a temporary measure I am going to use the symbol θ to represent the temperature measured on the ideal gas scale. I shall then define an *absolute* temperature scale, *T*, and show that it is identical with the ideal gas temperature scale.

To start with, I shall suppose that the working substance in our Carnot engine is an ideal gas. We shall refer to figure XI.1, in which *ab* and *cd* are isotherms at temperatures θ_2 and θ_1 respectively ($\theta_2 > \theta_1$), and *bc* and *da* are adiabats. Starting at the point $a(P_1, V_1)$, a quantity of heat Q_2 is supplied **to** the gas as it expands isothermally from *a* to $b(P_2, V_2)$ at temperature θ_2 on the ideal gas scale. During this phase, the cylinder is supposed to be uninsulated and placed in a hot bath at temperature θ_2. As it expands isothermally it does external work. Since the working substance is an ideal gas, the internal energy at constant temperature is independent of volume (there is no internal work against van der Waals forces to be done) so the heat supplied **to** the gas is equal to the external work that it does. That is, per mole,

$$Q_2 = R\theta_2 \ln(V_2/V_1). \tag{11.2.1}$$

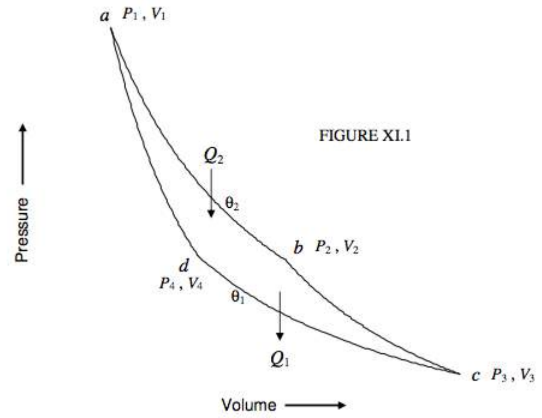


FIGURE XI.1

After the gas has reached b the cylinder is insulated and the gas expands adiabatically and reversibly to $c(P_3, V_3)$.

It is then placed in a cold bath at temperature θ_1, uninsulated, and compressed isothermally to $d(P_4, V_4)$. During this stage it gives out a quantity of heat Q_1:

$$Q_1 = R\theta_1 \ln(V_3/V_4). \tag{11.2.2}$$

Finally it is insulated again and compressed adiabatically and reversibly to its original state *a*.

For these four stages we have the equations

$$lP_1V_1 = P_2V_2 \tag{11.2.3}$$

$$P_2V_2^\gamma = P_3V_3^\gamma \tag{11.2.4}$$

$$P_3V_3 = P_4V_4 \tag{11.2.5}$$

$$P_1V_1^\gamma = P_4V_4^\gamma \tag{11.2.6}$$

From these, we readily see that

$$V_2/V_1 = V_3/V_4, \tag{11.2.7}$$

and therefore

$$Q_2/Q_1 = \theta_2/\theta_1. \tag{11.2.8}$$

The net heat received is $Q_2 - Q_1$, and this is the heat available for doing external work. A quantity of heat must be supplied at the beginning of each cycle, and so the efficiency of the cycle is

$$\eta = \frac{Q_2 - Q_1}{Q_2} = \frac{\theta_2 - \theta_1}{\theta_2}. \tag{11.2.9}$$

Thus the efficiency of the Carnot engine is the fractional temperature difference between source and sink.

We have specified in the above that the working substance is an ideal gas, the temperatures of source and sink being θ_1 and θ_2 on the ideal gas scale. Let us now not specify what the working substance is, but let us set up a system of 100 Carnot engines working in tandem, with the sink of one being the source for the next. We'll have the sink for the coldest engine in a bucket of melting ice (0 $^{\circ}$C) and the source for the hottest engine in a bucket of boiling water (100 $^{\circ}$C). They will be working between isothermals and adiabats on an absolute thermodynamic scale, *T*, defined such that the net work done by each engine (i.e. the area of each *PV* loop) per cycle is the same for each of the engines. This will define the temperature on an absolute scale. It would take me a while to use the computer to do a decent drawing of 100 isotherms and 2 adiabats, so I'm going to try to make do with a hand-drawn sketch (figure X1.2) of just five isotherms, two adiabats and four linked Carnot cycles to illustrate what I am trying to describe.

We suppose that the efficiency of such a Carnot engine depends solely on the temperature of source and sink:

$$Q_1/Q_2 = f(T_1, T_2). \tag{11.2.10}$$

We are making no assumption about the form of this function, which is completely arbitrary. We are free to define it in any manner that is useful to us in our attempt to define an absolute temperature scale.

FIGURE XI.2

Let us consider two adjacent engines, one working between temperatures T_1 and T_2, and the other working between temperatures T_2 and T_3. We have:

$$lQ_1/Q_2 = f(T_1, T_2) \tag{11.2.11}$$

$$Q_2/Q_3 = f(T_2, T_3) \tag{11.2.12}$$

and for the pair as a whole considered as a single engine,

$$Q_1/Q_3 = f(T_1, T_3). \tag{11.2.13}$$

From these we find that

$$f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_2, T_3)}. \tag{11.2.14}$$

This can be only if T_3 cancels from the right hand side, so that

$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)}. \tag{11.2.15}$$

That is,

$$\frac{Q_1}{Q_2} = \frac{\phi(T_1)}{\phi(T_2)}. \tag{11.2.16}$$

And since φ is a completely arbitrary function that we can choose at our pleasure to define an absolute scale, we choose

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \tag{11.2.17}$$

And, with this choice, the absolute thermodynamic temperature scale is identical with the ideal gas temperature scale. Equation 11.2.17 also implies that entropy in = entropy out. Entropy is conserved around the complete cycle. Entropy is a function of state.

In Sections 11.3 to 11.5 I give examples of some other cycles. These are largely for reference, and readers who wish to continue without interruption with the theoretical development of the subject can safely skip these and move on to Sections 11.7 and 11.8.

11.3: The Stirling Cycle

This takes place between two isotherms and two isochors. Note that, provided the working substance is an ideal gas, there is no change in the internal energy along the isotherms, and that the work done by or on the gas is equal to the heat gained by or lost from it. No work is done along the isochors. I show the cycle in the PV plane in figure XI.3, and an imaginary schematic engine in figure XI.4.

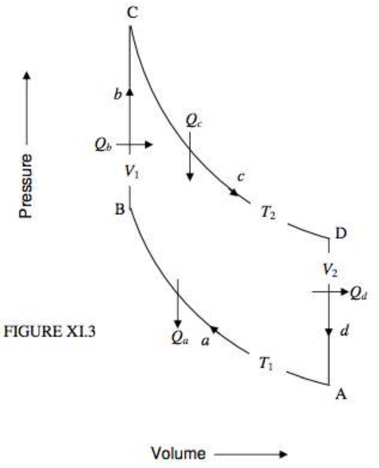


FIGURE XI.3

$$Q_a = RT_1 \ln(V_2/V_1)$$

$$Q_b = C_V(T_2 - T_1)$$

$$Q_c = RT_2 \ln(V_2/V_1)$$

$$Q_d = C_V(T_2 - T_1)$$

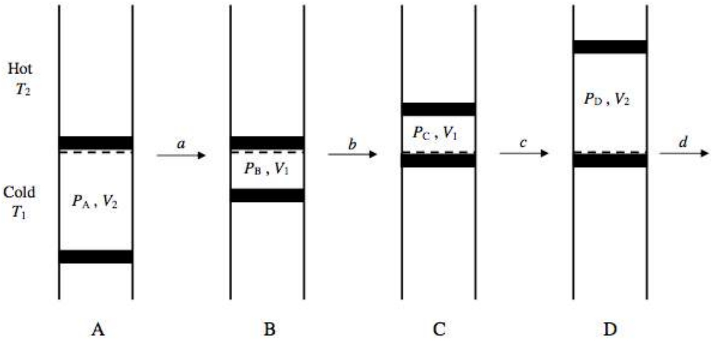


FIGURE XI.4

The gas is supposed to be held in a cylinder between two pistons. The cylinder is divided into two sections by a porous partition. One section is kept at a hot temperature T_2 and the other is kept at a cold temperature T_1.

In stage a, the cold gas is compressed isothermally. The work done **on** a mole of the gas is $RT_1 \ln(V_2/V_1)$; this is converted into heat, Q_a, which is lost from the gas to the cold reservoir.

In stage b, the gas, held at constant volume, is transferred to the hot reservoir. No work is done on or by the gas, but a quantity of heat $Q_b = C_V(T_2 - T_1)$ per mole is supplied to the gas.

In stage c, the hot gas is expanded isothermally to its original volume. The work done by a mole of the gas is $RT_2 \ln(V_2/V_1)$; in order to prevent the gas from cooling down, it has to absorb an equal amount of heat, Q_c **from** the hot reservoir. Note that $Q_c > Q_a$.

In stage d, the gas, held at constant volume, is transferred back to the cold reservoir. No work is done on or by the gas, but the gas loses a quantity of heat $Q_d = C_V(T_2 - T_1)$ to the cold reservoir. Note that $Q_d = Q_b$.

Exercise: Show that the efficiency is

$$\eta = \frac{R(T_2 - T_1)\ln(V_2/V_1)}{C_V(T_2 - T_1) + RT_2 \ln(V_2/V_1)}. \tag{11.3.1}$$

If the gas is an ideal diatomic gas (to which air is an approximation), then $C_V = \frac{5}{2}R$, and then

$$\eta = \frac{(T_2 - T_1)\ln(V_2/V_1)}{2.5\,(T_2 - T_1) + T_2\ln(V_2/V_1)}\,. \tag{11.3.2}$$

If helium were used as an ideal gas, the efficiency would be greater, because for helium, $C_V = \frac{3}{2}R$.

11.4: The Otto Cycle

The Otto cycle (to which the engine under the hood of your car bears some slight resemblance) works between two isochors and two adiabats (figure XI.5).

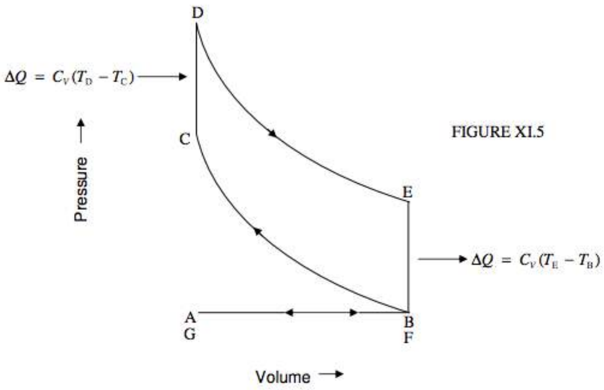


FIGURE XI.5

The cycle starts at A. From A to B the piston recedes and a valve is open, so that a misture of air and petrol (gasoline) is drawn in at constant (atmospheric) pressure. The temperature is typically somewhat above ambient temperature because of the previous operation of the cycle. At B, the valve is closes, and now from B to C a fixed mass of gas is compressed adiabatically, the temperature being a few hundred K. C is the point of maximum compression. At this point a spark is struck and the mixture is ignited. In effect heat is added to the system and the temperature goes up instantaneously to perhaps 2000 K at constant (small) volume. The gas, now having reached D, expands adiabatically to E, doing work, and the temperature drops somewhat. At E, a (second) valve opens, gas is expelled, the pressure drops to atmospheric, and the temperature drops to its original value. We are now at F. The piston pushes the remaining gas out, and we end at G. The cycle starts anew.

It is left as an exercise to show:

Net work done by the engine per cycle = $C_V\left(T_{\mathrm{D}}-T_{\mathrm{C}}\right)\left(1-\frac{T_{\mathrm{B}}}{T_{\mathrm{C}}}\right)$.

Volume of stroke = $V_{\mathrm{B}}-V_{\mathrm{C}}=V_{\mathrm{B}}\left[1-\left(\frac{T_{\mathrm{B}}}{T_{\mathrm{C}}}\right)^{1/\gamma-1)}\right]$.

Maximum pressure = $P_{\mathrm{D}}=P_{\mathrm{B}}\frac{T_{\mathrm{D}}}{T_{\mathrm{B}}}\left(\frac{T_{\mathrm{C}}}{T_{\mathrm{B}}}\right)^{1/(\gamma-1)}$.

Efficiency = $1-\left(\frac{V_C}{V_{\mathrm{B}}}\right)^{\gamma-1}=1-\frac{T_{\mathrm{B}}}{T_{\mathrm{C}}}$.

In principle the efficiency could be very large if the temperature at C, at the end of the adiabatic compression, were high. In practice the temperature at the end of the adiabatic compression is limited (and therefore so is the efficiency) because, if the temperature were too high, the air-gasoline mixture would ignite spontaneously.

11.5: The Diesel Cycle

This difficulty is avoided in the Diesel cycle in that, during the adiabatic compression stage to a high temperature, it is just air (not an air-fuel mixture) that is compressed. Only then, when the temperature is high, is fuel injected, which then immediately ignites. The cycle is shown in figure XI.6.

We start at A. A valve opens and the piston moves back, and pure air (no fuel) is sucked into the cylinder. This is followed by an adiabatic compression from B to C, which can reach a high temperature of 2000 K or so. At C a jet of liquid fuel is forced at high pressure into the cylinder by a pump that is operated by the engine itself. The fuel immediately ignites. The rate of injection is held so that the mixture expands at constant pressure until we reach D, at which point the injection of fuel is cut off and the gas expands adiabatically to E. A valve is then opened so that the pressure drops to atmospheric at F. The piston then pushes the remainder of the mixture out, and the cycle stars anew.

It is left as an exercise to show:

Net work done by the engine per cycle = $C_P\left[T_\text{D}-T_\text{B}\left(\frac{P_\text{C}}{P_\text{B}}\right)^{1-1/\gamma}\right]-C_V\left[T_\text{D}\left(\frac{P_\text{B}}{P_\text{C}}\frac{T_\text{P}}{T_\text{B}}\right)^{\gamma-1}-T_\text{B}\right]$.

Volume of stroke = $V_\text{B}-V_\text{C}=V_\text{B}\left[1-\left(\frac{P_\text{B}}{P_\text{C}}\right)^{1/\gamma}\right]$.

Efficiency = $1-\frac{C_\text{V}\left[T_\text{D}\left(\frac{P_\text{B}}{P_\text{C}}\frac{T_\text{D}}{T_\text{B}}\right)^{\gamma-1}-T_\text{B}\right]}{C_P\left[T_\text{D}-T_\text{B}\left(\frac{P_\text{C}}{P_\text{B}}\right)^{1-1/\gamma}\right]}$.

Have a look at http://www.univ-lemans.fr/enseignements/physique/02/thermo/diesel.html

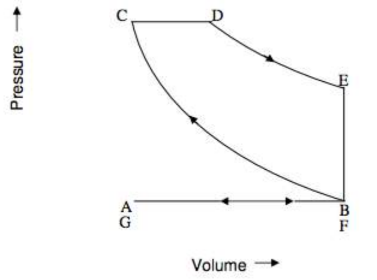


FIGURE XI.6

Exercise: Assuming γ = 1.4, what are the efficiencies of the Carnot, Otto and Diesel cycles running between 350 K and 2000 K? Assume for the Diesel cycle that the maximum pressure is 30 atmospheres. Assume for the Otto cycle that T_C =650 K.

11.6: The Rankine Cycle (Steam Engine)

The *Titfield Thunderbolt* runs on an engine that slightly resembles the Rankine cycle.

The amount of work obtainable from an engine depends on the amount of the working substance and on the temperature. Internal combustion Otto and Diesel engines work at high temperatures, so they can be small. The steam engine is bulky but does not require high temperatures. The steam engine has a *boiler* (which, naturally, boils water into steam) and a *condenser* (which, naturally, condenses the steam back again to water).

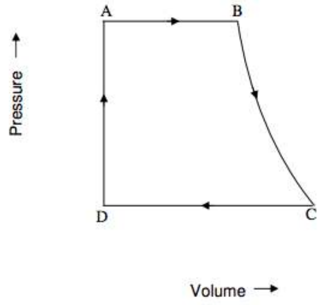


FIGURE XI.7

Steam from the boiler is drawn into a cylinder at constant pressure (A to B), at which point the intake valve is closed and the remaining expansion (B to C) is adiabatic, taking the temperature down to the temperature of the condenser. The section C to D corresponds to the condensation of the steam. From D to A the condensed water is transferred to the boiler, and the cycle starts again.

11.7: A Useful Exercise

It would probably *not* be a useful exercise to try to memorise the details of the several heat engine cycles described in this chapter. What probably would be a useful exercise is as follows. Note that in each cycle there are four stages, which, in principle at least (if not always in practice) are well defined and separated one from the next. These stages are described by one or another of an isotherm, an adiabat, an isochor or an isobar. It would probably be a good idea to ask oneself, for each stage in each engine, the values of ΔQ, ΔW and ΔU, noting, of course, that in each case, $\Delta U = \Delta Q + \Delta W$. In each case take care to note whether heat is added to or lost from the engine , whether the engine does work or whether work is done on it, and whether the internal energy increases or decreases. By doing this, one could then easily determine how much heat is supplied to the engine, and how much net work it does during the cycle, and hence determine the efficiency of the engine.

The following may serve as useful guidelines. In these guidelines it is assumed that any work done is reversible, and that (except for the steam engine or Rankine cycle) the working substance may be treated as if it were an ideal gas.

Along an *isotherm*, the *internal energy* of an ideal gas is unchanged. That is to say, $\Delta U = 0$. The work done (per mole of working substance) will be an expression of the form $RT \ln(V_2/V_1)$, and the heat lost or gained will then be determined by $\Delta Q + \Delta W = 0$.

Along an *adiabat*, no heat is gained or lost, so that $\Delta Q = 0$. The expression for the work done per mole will be of the form $\frac{R(T_1-T_2)}{\gamma-1} = \frac{P_1V_1-P_2V_2}{\gamma-1}$ where V is the molar volume. Just be sure to understand whether work is done on or by the engine. The change in the internal energy (be sure to understand whether it is an increase or a decrease) is then given by $\Delta U = \Delta W$.

Along an *isochor*, no work is done. That is, $\Delta W = 0$. The heat lost or gained per mole will be of an expression of the form $C_V(T_2 - T_1)$, where C_V is the molar heat capacity at constant volume. The change in the internal energy (be sure to understand whether it is an increase or a decrease) is then given by $\Delta U = \Delta Q$.

Along an *isobar*, none of Q, W or U are unchanged. The work done per mole (*by* or *on* the engine?) will be an expression of the form $\Delta W = P(V_2 - V_1) = R(T_2 - T_1)$.

The heat added to or lost from the engine will be an expression of the form $C_P(T_2 - T_1)$, where C_P is the molar heat capacity at constant pressure. The change in the internal energy (be sure to understand whether it is an increase or a decrease) is then given by $\Delta U = \Delta Q + \Delta W$.

It might also be a good idea to try to draw each cycle in the $T : S$ plane (with the intensive variable T on the vertical axes). Indeed I particularly urge you to do this for the Carnot cycle, which will look particularly simple. Note that, while the *area* inside the cycle in the *$P : V$ plane* is equal to the net work done on the engine during the cycle, the *area* inside the cycle in the $T : S$ plane is equal to the *net heat* supplied to the engine during the cycle.

11.8: Heat Engines and Refrigerators

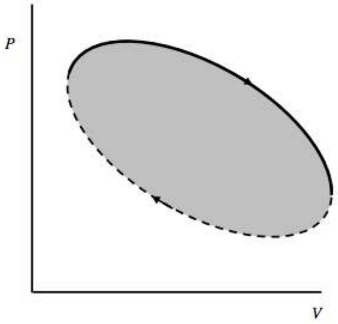


FIGURE XI.8

Figure XI.8 illustrates schematically the path taken by the state of a working substance is a generalized heat engine. In the upper part of the cycle (continuous curve) the working substance is expanding, and the machine is doing work. The work done **by** the engine is ∫*PdV*, or the area under that part of the curve. In the lower part of the cycle (dashed curve) the working substance is being compressed; work is being done **on** it. This work is the area under the dashed portion of the cycle. The ***net*** work done **by** the engine during the cycle is the work done **by** the engine while it is expanding *minus* the work done **on** it during the compression part of the cycle, and this is the *area enclosed* by the cycle.

During one part of any heat engine cycle, heat is supplied **to** the engine, and during other parts, heat is lost **from** it. As described in Section 11.1, the *efficiency* η of a heat engine is defined by

$$\eta=\frac{\textbf{net}\text{ external work done }\textbf{by}\text{ the engine during a cycle}}{\text{heat supplied }\textbf{to the engine during a cycle.}} \tag{11.8.1}$$

Note that the word “net” does not appear in the denominator. The efficiency can also be *calculated* from

$$\eta=\frac{Q_{\text{ in }}-Q_{\text{ out }}}{Q_{\text{ in }}}, \tag{11.8.2}$$

though I stress that this is not a *definition*.

In the *Carnot engine*, which is the most efficient conceivable engine for given source and sink temperature, the efficiency is

$$\eta=\frac{T_2-T_1}{T_2}, \tag{11.8.3}$$

where T_2 and T_1 are respectively the temperatures of the hot source and cold sink.

If the working substance is taken round a cycle in the *PV*-plane in the *counterclockwise* direction, the device is a *refrigerator*.

In that case the area enclosed by the cycle is equal to the net work that is done **on** the working substance. If the refrigerator operates on a reverse *Carnot* cycle, the working substance **takes in** (from whatever it is that it is trying to cool) a quantity of heat Q_1 as it expands isothermally from *d* to *c* (see figure XI.1, but with the arrows reversed) and **expels** *a* (greater) quantity of heat Q_2 as it is compressed isothermally from *b* to *a*. This quantity Q_2 is expelled into the room – which is why the room gets warmer when you switch on the fridge. (What – you never noticed?) The *refrigerating effect* is Q_1, since this is the quantity of heat taken in by the refrigerator from the body that is to be cooled.

The *coefficient of performance* of a refrigerator is defined by

$$\frac{\text{refrigerating effect}}{\text{net work done }\textbf{on}\text{ the engine during the cycle.}} \tag{11.8.4}$$

By the first law of thermodynamics, the denominator of the expression is $Q_2 - Q_1$, and for a reversible Carnot cycle, the entropy in equals the entropy out, so that $Q_2/Q_1 = T_2/T_1$. Therefore the coefficient of performance for a Carnot refrigeration cycle can be calculated from

$$\frac{T_1}{T_2-T_1}. \tag{11.8.5}$$

This, of course, can be much greater than 1 – but no refrigerator working between the same source and sink temperatures can have a coefficient of performance greater that that of a reversible Carnot refrigerator.

Of course the working substance in a real refrigerator (“fridge”) is not an ideal gas, nor does one follow a Carnot cycle – there are too many practical difficulties in the way of achieving this ideal dream. As mentioned elsewhere in this course, I am not a practical man and I am not suited to describing real, practical machines. The fundamental principles described in this section do, of course, still apply in the real world! In a real refrigerator, the working substance (the *refrigerant*) is a volatile fluid which is vaporized in one part of the operation and condensed to a liquid in another part. In industrial refrigerators, the refrigerant may be ammonia, but this is considered to be too dangerous for domestic use. “Freon”, which was a mixture of chlorofluorocarbons, such as CCl_2F_2, was in fashion for a while, but escaping chlorofluorocarbons have been known for some time to cause breakdown of ozone (O_3) in the atmosphere, thus destroying our protection against ultraviolet radiation from the Sun. The chlorofluorocarbons have been largely replaced by hydrofluorocarbons, such as $C_2H_2F_4$, which are believed to be less damaging to the ozone layer. The exact formula or mixture is doubtless a trade secret.

The fluid is forced around a system of tubes by a pump called the *compressor*. Shortly before the fluid reaches the freezer it is in liquid form, moving along some rather narrow pipes. It is then forced through a nozzle into a system of wider pipes (the *evaporator*) surrounding the freezer, and there it vaporizes, taking heat from the food and from the air in the freezer. A fan may also distribute the cooled air throughout the rest of the refrigerator. After leaving the freezer, the vapour returns to the compressor, where it is, of course, compressed (which is why the pump is called the compressor). This produces heat, which is dissipated into the room as the fluid is forced through a series of pipes and vanes, known as the condenser, at the rear of the fridge, where the fluid condenses into liquid form again. The cycle then starts anew.

The following summary of Carnot heat engines and refrigerators may be helpful. (But just remember that, while Carnot cycles are the most efficient engines and refrigerators for given source and sink temperatures, the practical realization of a real engine or refrigerator may not be identical to this theoretical ideal.)

Notation:

T_2 = hotter temperature

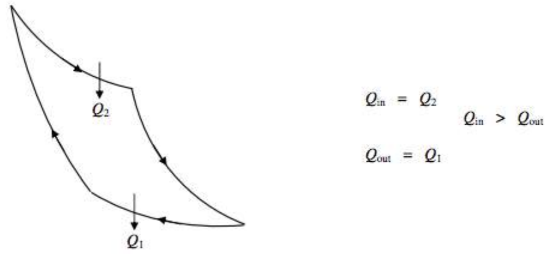
T_1 = cooler temperature

Q_2 = heat gained or lost at T_2

Q_1 = heat gained or lost at T_1

$\Delta S = 0 \qquad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

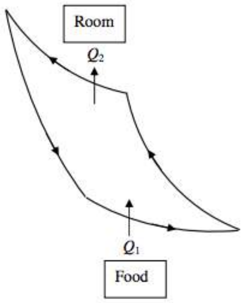
Heat Engine:



$$\Delta U = 0 \quad \text{Net work done } \textbf{by} \text{ engine } = Q_2 - Q_1.$$

$$\text{Efficiency } \eta = \frac{Q_{in} - Q_{\text{ out}}}{Q_{\text{ in}}} = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

Refrigerator:



$Q_{\text{in}} = Q_1$ $\quad Q_{\text{out}} > Q_{\text{in}}$

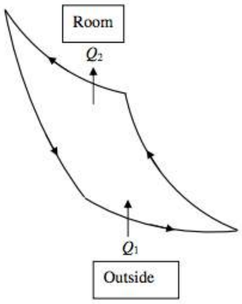
$Q_{\text{out}} = Q_2$

$$\Delta U = 0 \qquad \text{Net work done } \textbf{on} \text{ refrigerator } = Q_2 - Q_1$$

$$\text{Coefficient of Performance } P = \frac{Q_{\text{ in}}}{Q_{\text{ oxt}} - Q_{\text{ in}}} = \frac{Q_1}{Q_2 - Q_1} = \frac{T_1}{T_2 - T_1}$$

Heat Pump:

The principle of a heat pump is the same as that of a refrigerator, except that its purpose is different. The purpose of a refrigerator is to extract heat from something (e.g. food) and so to make it colder. That the heat so extracted goes into the room to make the room warmer (at least in principle) is incidental. The important thing is how much heat is extracted from the food, and that is why it is appropriate to define the coefficient of performance of a refrigerator as the *refrigerating effect* (i.e. Q_1) divided by the net work done on the refrigerator, per cycle. But with a heat pump, the object is to *heat the room* by extracting heat from outside. That the outside may become cooler (at least in principle) is incidental. Thus, for a heat pump, the appropriate definition of the coefficient of performance is the *heating effect* (i.e. Q_2) divided by the net work done on the refrigerator, per cycle.



$Q_{\text{in}} = Q_1$ $\quad Q_{\text{out}} > Q_{\text{in}}$

$Q_{\text{out}} = Q_2$

$$\Delta U = 0 \qquad \text{Net work done } \textbf{on} \text{ heat pump } = Q_2 - Q_1$$

$$\text{Coefficient of Performance } P = \frac{Q_{\text{out}}}{Q_{\text{out}} - Q_{\text{in}}} = \frac{Q_2}{Q_2 - Q_1} = \frac{T_2}{T_2 - T_1}$$

You can see from this equation that, the warmer it is outside (T_1), the greater the coefficient of performance. You may therefore wonder if it is practical to use a heat pump to heat a building in a cold climate, such as the Quebec winter. And, if it isn't, can one devise an engine that is simultaneously a refrigerator and a heat pump; that is to say, it extracts heats from (i.e. cools) the food, and transfers this heat (plus a little bit more because of the work that is done on the refrigerator/heat pump) into the room in order to heat the room effectively. There's an answer to that in an article in the Victoria Times-Colonist of June 11, 2006, which I reproduce, with permission, below.

Fridge used to heat

Energy-efficient heating allows supermarket to stay warm during bone-chilling winters

BY MIKE DE SOUZA
CanWest News Service

OTTAWA— The manager of a large grocery supermarket in Quebec was skeptical when Natural Resources Canada told him he could run his 9,450-square-metre store during bone-chilling winters without a furnace.

Heading into the Christmas holiday season in 2004, government researchers helped design the brand new grocery store for Loblaws, in Repentigny, northeast of Montreal, with a unique, revolutionary system that allows it to use its refrigerators to heat the building.

"In December, and the months that followed the opening in 2004, it was an especially cold period, -26 C and -30 C," said Dr. Sophie Hosatte, a senior NRCan researcher.

"It's a critical period for the supermarket in terms of sales, [but] there was absolutely no problem. The comfort-level was excellent inside the supermarket."

More than two years later, the system continues to keep the store running through winters, capturing heat and energy released by the refrigerators and pumping it back into the building. As a result it drastically slashes costs for heating and maintenance, as well as reducing greenhouse gas emissions, Hosatte said.

In a single store, NRCan estimates the system can cut greenhouse gas emissions by 1.5 megatonnes, the equivalent of 300 cars driving 20,000 kilometres in a year. But since the new government is in the midst of reviewing all climate-change programs and policies developed when the federal Liberals were in power, the future of the technology is in limbo.

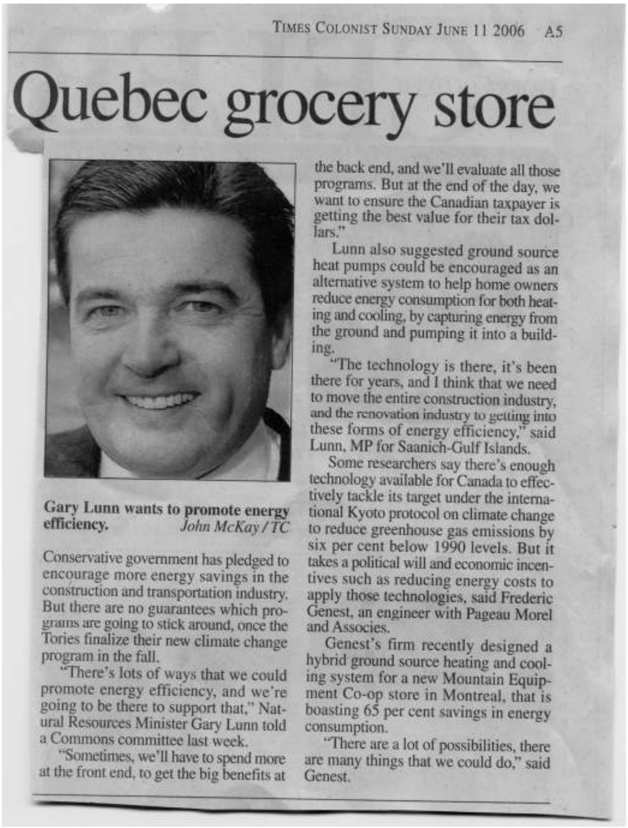
"We are in a transition year," Hosatte said. "For the future, we have to wait for the new climate change plan."

NRCan continuously monitors and measures the performance of the system throughout the Repentigny store, and so far, Hosatte said the results are meeting their targets perfectly. The technology has also been adapted in two Loblaws grocery stores that retrofitted their heating systems in the Ottawa area, along with about a dozen ice rinks and arenas across the country.

While her department has demonstrated the system works well, she said it still needs to provide more technical support to help private sector partners apply and adapt the technology.

"That's our role, presently, to develop tools, guidelines and to help supermarkets adapt these technologies," she said. "Otherwise there would be reluctance because of the risk."

The researchers may take comfort the



TIMES COLONIST SUNDAY JUNE 11 2006 A5

Quebec grocery store

Gary Lunn wants to promote energy efficiency. *John McKay / TC*

Conservative government has pledged to encourage more energy savings in the construction and transportation industry. But there are no guarantees which programs are going to stick around, once the Tories finalize their new climate change program in the fall.

"There's lots of ways that we could promote energy efficiency, and we're going to be there to support that," Natural Resources Minister Gary Lunn told a Commons committee last week.

"Sometimes, we'll have to spend more at the front end, to get the big benefits at the back end, and we'll evaluate all those programs. But at the end of the day, we want to ensure the Canadian taxpayer is getting the best value for their tax dollars."

Lunn also suggested ground source heat pumps could be encouraged as an alternative system to help home owners reduce energy consumption for both heating and cooling, by capturing energy from the ground and pumping it into a building.

"The technology is there, it's been there for years, and I think that we need to move the entire construction industry, and the renovation industry to getting into these forms of energy efficiency," said Lunn, MP for Saanich-Gulf Islands.

Some researchers say there's enough technology available for Canada to effectively tackle its target under the international Kyoto protocol on climate change to reduce greenhouse gas emissions by six per cent below 1990 levels. But it takes a political will and economic incentives such as reducing energy costs to apply those technologies, said Frederic Genest, an engineer with Pageau Morel and Associes.

Genest's firm recently designed a hybrid ground source heating and cooling system for a new Mountain Equipment Co-op store in Montreal, that is boasting 65 per cent savings in energy consumption.

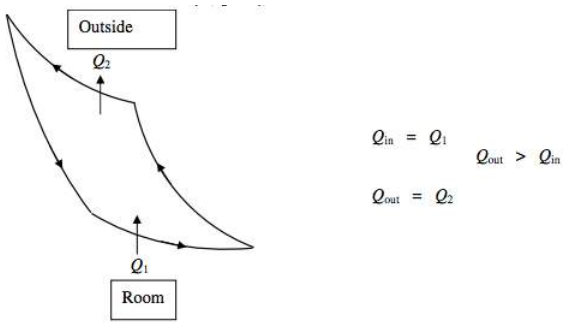
"There are a lot of possibilities, there are many things that we could do," said Genest.

Air Conditioner

The purpose of a *refrigerator* ("fridge") is to pump some heat Q_1 from the food (or whatever is to be kept cool). The quantity Q_1 is the "refrigerating effect". During the operation of the fridge, a somewhat greater quantity Q_2 of heat is expelled into the room, though this should not result in a very noticeable rise in temperature of the room, partly because the room has a large thermal capacity, and partly because much of this heat will be lost through the windows. The *coefficient of performance* of the fridge is the refrigerating effect per cycle, Q_1, divided by the net work done on the fridge per cycle, and, for a Carnot cycle it can be calculated from $T_1/(T_2 - T_1)$.

The purpose of a *heat pump* is to pump some heat Q_1 from outside, and (from the work done on the pump) to pump a larger quantity Q_2 of heat into the room – large enough, indeed to warm the room appreciably, supposing that you don't keep all the windows wide open. The coefficient of performance must therefore be defined as Q_2 divided by the net work done on the fridge per cycle. For a Carnot cycle it can be calculated from $T_2/(T_2 - T_1)$.

There is a third possibility, namely an air conditioner. This will incorporate a dehumidifier, but, in our present context we regard it as a device whose purpose is to pump heat from the room to the outside, rather than from outside to the room. If it is successful, the room will become cooler than the outside. Thus an air conditioner is more like a refrigerator, in that the coefficient of performance is the heat Q_1 extracted per cycle from the room divided by the net work done on the machine per cycle. For a Carnot cycle it can be calculated from $T_1/(T_2 - T_1)$.



$$\Delta U = 0 \qquad \text{Net work done } \textbf{on} \text{ air conditioner } = Q_2 - Q_1 \ .$$

$$\text{Coefficient of Performance } P = \frac{Q_{\text{ in}}}{Q_{\text{ out}} - Q_{\text{ in}}} = \frac{Q_1}{Q_2 - Q_1} = \frac{T_1}{T_2 - T_1} \ .$$

Those who have read thus far will have an idea that there are things called *heat engines*, *refrigerators*, *heat pumps and air conditioners*, which are represented by Carnot cycles or similar cycles, with arrows going in different directions, a few equations with different subscripts, and subtly different definitions of efficiency or coefficient of performance. Since I prepared these notes I have discovered that there actually exist in the real world, real, solid machines called *heat engines*, *refrigerators*, *heat pumps and air conditioners*. I have discovered two very nice little pamphlets describing real heat pumps and real air conditioners, and how you might install them to heat or to cool your home. They are called *Heating and Cooling with a Heat Pump*, and *Air Conditioning your Home*, each about 50 pages. My copies are dated 1996, revised 2004, though I dare say you might be able to get more recent ones. They are available free from Energy Publications, Office of Energy Efficiency, Natural Resources Canada, c/o S.J.D.S., 1779 Pink Road, Gatineau, Province of Québec, Canada J9J 3N7. I found them fascinating.

11.9: Entropy is a Function of State

We have defined temperature on the absolute scale such that the temperature of the source of a reversible Carnot heat engine is proportional to the heat taken in by the engine during its isothermal expansion at the hot temperature, and the temperature of the sink is proportional to the heat lost by the engine during its isothermal compression at the cool temperature. No heat is gained or lost, of course, during the adiabatic phases, and there is no change in internal energy over a complete cycle. Therefore $Q_1/Q_2 = T_1/T_2$.

Now, any cycle can be represented by an infinite number of infinitesimally narrow Carnot cycles operating in tandem. Thus $\int dQ/T$ during that part of the cycle in which an engine is losing heat is equal to $\int dQ/T$ during that part of the cycle in which it is absorbing heat. Therefore, during the complete cycle, $\int dQ/T$ is zero. This means that the net change in entropy during a complete cycle is zero, so that entropy is a function of state. In effect $1/T$ is an *integrating factor* which, when it multiplies the inexact differential $đQ$, results in the exact differential $đQ/T = dS$.

CHAPTER OVERVIEW

12: Free Energy

12.1: Review of Internal Energy and Enthalpy

We are by now familiar with the equations

$$dU = TdS - PdV \text{ and } dH = TdS + VdP,$$

and with the ideas that the increase in the internal energy is the heat added at constant volume and the increase in enthalpy is the heat added at constant pressure, and that U is constant in an adiabatic isochoric process and H is constant in an adiabatic isobaric process. I am now going to examine these equations and statements a bit more critically. In particular I am going to consider that there may be several types of configuration work involved in addition to just PdV work of compression or expansion.

The First Law of thermodynamics is $dU = dQ + dW$.

The work done on a system may comprise an irreversible component dW_I (such as stirring with a paddle, or forcing an electric current through a resistor) plus some reversible components dW_R. The irreversible component is dissipated as heat and is tantamount to adding heat to the system. The heat and the irreversible work contribute to the increase in entropy of the system, according to $dS = (dQ + dW_I)/T$. Thus we have $dQ = TdS - dW_I$.

The reversible component of the work may consist of work done in compressing the system, $-PdV$, but there may also be other kinds of work, such as the work required to create new area, $\Gamma d\sigma$, or the work required to twist a rod, $\tau d\theta$, or the work required to charge a battery, Edq, or the work required to magnetize a specimen, BdM, and perhaps others. In general the expression for each of these forms of reversible work is of the form XdY, where X is an intensive state variable and Y is an extensive state variable. All of these forms of nondissipative work can collectively be called *configuration work*.

The total work done on the system is therefore of the form

$$dW = dW_I - PdV + \sum XdY. \tag{12.1.1}$$

The first law therefore takes the form

$$dU = dQ + dW_I - PdV + \sum XdY. \tag{12.1.2}$$

If the system is held at constant volume (e.g. in a pressure cooker or in an autoclave), then no PdV work of expansion or compression is done. And if no other sort of work is done either (either non-PdV reversible work or irreversible work dW_I) then the increase in internal energy of the system is just equal to the heat added to it.

Enthalpy is defined as $H = U + PV$, so that $dH = dU + PdV + VdP$. From this, we obtain

$$dH = dQ + dW_I + VdP + \sum XdY. \tag{12.1.3}$$

If heat is added to a system at constant pressure, then the system expands and does external work. However, provided that the pressure is held constant and if no other sort of work is done either (either non-PdV reversible work or irreversible work dW_I) then the increase in the enthalpy of the system is just equal to the heat added to it.

In summary, the well-known equations $dU = TdS - PdV$ and $dH = TdS + VdP$ are valid for reversible and for irreversible processes, provided that the only nondissipative work is PdV work; but in general, if there are other types of work being done (e.g. $\Gamma d\sigma$, or $\tau d\theta$, etc.), the required relations are

$$dU = TdS - PdV + \sum XdY \tag{12.1.4}$$

and

$$dH = TdS + VdP + \sum XdY. \tag{12.1.5}$$

12.2: Free Energy

We shall be learning that there are two sorts of *free energy*.

There is the *Helmholtz free energy*. Commonly used symbols for this are A (from the German *die Arbeit* – work) or F.

And there is the *Gibbs free energy*. Commonly used symbols for this are $G-$ or F!

It is unfortunate that some writers will use simply the term "free energy”, using the symbol F, without specifying which, or even giving evidence that they are aware of the difference. I have seen the symbol F used about equally often for Helmholtz, Gibbs or unspecified free energies.

In these notes I shall use the symbol A for the Helmholtz free energy and G for the Gibbs free energy, and I shall avoid the symbol F.

12.3: Helmholtz Free Energy

The Helmholtz free energy A is defined as

$$A = U - TS. \tag{12.3.1}$$

As when we first defined enthalpy, this doesn't seem to mean much until we write it in differential form:

$$dA = dU - TdS - SdT. \tag{12.3.2}$$

On substitution from equation 12.1.6 ($dU = TdS - PdV + \sum XdY$), this becomes

$$dA = -SdT - PdV + \sum XdY. \tag{12.3.3}$$

This tells us that in an isothermal process (in which $dT = 0$), the **increase** in the Helmholtz function of a system is equal to all the reversible work ($-PdV + \sum XdY$) done **on** it. Conversely, if a machine does any reversible work at constant temperature, the Helmholtz function decreases, and the **decrease** in the Helmholtz function is equal (if the temperature is held constant) to the reversible work (of all types) done **by** the machine. It is in this sense that the Helmholtz function is called the “free energy”. It is the energy, so to speak, that is free for the performance of external reversible (i.e. useful) work.

12.4: Gibbs Free Energy

The Gibbs free energy G is defined as

$$G=H-TS \tag{12.4.1}$$

or, what amounts to the same thing,

$$G=A+PV. \tag{12.4.2}$$

As when we first defined enthalpy, this doesn't seem to mean much until we write it in differential form:

$$dG=dH-TdS-SdT \tag{12.4.3}$$

or

$$dG=dA+PdV+VdP. \tag{12.4.4}$$

Then, either from equations 12.1.5 ($dH = TdS + VdP + \sum XdY$) and 12.5.3 or from equation 12.4.3 ($dA = -SdT - PdV + \sum XdY$) and 12.5.4, we obtain

$$dG=-SdT+VdP+\sum XdY \tag{12.4.5}$$

That is to say that, if the temperature and pressure are constant, the increase in the Gibbs function of a system is equal to the reversible work (other than *PdV* work of compression) done on it. Conversely, if the temperature and pressure are held constant, and a machine is used to do external work (which may include but is not limited to *PdV* work of expansion), the Gibbs function decreases by the amount of reversible (i.e.useful) work done by the machine other than the *PdV* work of expansion.

12.5: Summary, the Maxwell Relations, and the Gibbs-Helmholtz Relations

$$dU = TdS - PdV + \sum XdY \tag{12.5.1}$$

$$dH = TdS + VdP + \sum XdY \tag{12.5.2}$$

$$dA = -SdT - PdV + \sum XdY \tag{12.5.3}$$

$$dG = -SdT + VdP + \sum XdY \tag{12.5.4}$$

If the only reversible work done on or by a system is PdV work of expansion or compression, we have the more familiar forms

$$dU = TdS - PdV \tag{12.5.5}$$

$$dH = TdS + VdP \tag{12.5.6}$$

$$dA = -SdT - PdV \tag{12.5.7}$$

$$dG = -SdT + VdP \tag{12.5.8}$$

All four thermodynamic functions are functions of state (and hence their differentials are exact differentials) and therefore

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \tag{12.5.9}$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V \tag{12.5.10}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \tag{12.5.11}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \tag{12.5.12}$$

Further, by equating the mixed second derivatives, we obtain the four Maxwell Thermodynamic Relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{12.5.13}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{12.5.14}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{12.5.15}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{12.5.16}$$

The Gibbs-Helmholtz Relations are trivially found from $A = U - TS$ and together with equations 12.6.11a and 12.6.12a. $G = H - TS$ They are

$$U = A - T\left(\frac{\partial A}{\partial T}\right)_V \tag{12.5.17}$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P \tag{12.5.18}$$

12.6: The Joule and Joule-Thomson Coefficients

In Chapter 10, we studied the Joule and Joule-Thomson experiments and we calculated the Joule and Joule-Thomson coefficients. Now that we are familiar with the Helmholtz and Gibbs functions, and, in particular, with two Maxwell relations that can be derived from them, we can obtain alternative derivations for these two coefficients. These may be easier than the derivations we gave in Chapter 10. I am indebted to Dr Greg Trayling for the derivation of the Joule coefficient; the derivation of the Joule-Thomson coefficient follows a parallel argument.

Let us start with the *Joule coefficient*. Here we are interested in how the temperature changes with volume in an experiment in which the internal energy is constant. That is, we want to derive the Joule coefficient, $\eta = (\partial T/\partial V)_U$.

Now entropy is a function of state – i.e. of the intensive state variables *P*, *V* and *T*. (*V* = molar volume.) But the intensive state variables for a particular substance are related by an equation of state, so we need express the entropy as a function of only two of *P*, *V* or *T*, and, since we are seeking a relation between *V* and *T*, let us choose to express *S* as a function of *V* and *T*, so that

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT. \tag{12.6.1}$$

Let us look at these three terms in turn.

First, *dS*. In the Joule experiment, the internal energy of the gas is constant, so that

$$TdS - PdV = 0. \tag{12.6.2}$$

That is,

$$dS = \frac{PdV}{T}. \tag{12.6.3}$$

For the first term on the right hand side of equation 12.7.1, we make use of the Maxwell relation, equation 12.6.15, which we derived from the Helmholtz function:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V. \tag{12.6.4}$$

For the second term on the right hand side we obtain

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_v \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \Big/ \left(\frac{\partial U}{\partial S}\right)_V = \frac{C_v}{T}. \tag{12.6.5}$$

Thus, equation 12.7.1 becomes

$$\frac{PdV}{T} = \left(\frac{\partial P}{\partial T}\right)_V dV + \frac{C_V dT}{T}. \tag{12.6.6}$$

Multiply through by *T*, and divide by *dV*, taking the infinitesimal limit as *dV* → 0, recalling that we are dealing with an experiment in which the internal energy is constant, and we arrive at

$$P = T\left(\frac{\partial P}{\partial T}\right)_V + C_V\left(\frac{\partial T}{\partial V}\right)_U, \tag{12.6.7}$$

from which we immediately obtain

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right], \tag{12.6.8}$$

quod erat demonstrandum.

Let us now consider the *Joule-Thomson coefficient*. Here we are interested in how the temperature changes with pressure in an experiment in which the enthalpy is constant. That is, we want to derive the Joule-Thomson coefficient, $\mu = (\partial T/\partial P)_H$.

Now entropy is a function of state – i.e. of the intensive state variables *P*, *V* and *T*. (*V* = molar volume.) But the intensive state variables for a particular substance are related by an equation of state, so we need express the entropy as a function of only *two* of

P, *V* or *T*, and, since we are seeking a relation between *P* and *T*, let us choose to express *S* as a function of *P* and *T*, so that

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT. \tag{12.6.9}$$

Let us look at these three terms in turn.

First, *dS*. In the Joule-Thomson experiment, the enthalpy of the gas is constant, so that

$$TdS + VdP = 0. \tag{12.6.10}$$

That is,

$$dS = -\frac{VdP}{T}. \tag{12.6.11}$$

For the first term on the right hand side of equation 12.7.9, we make use of the Maxwell relation, equation 12.6.16, which we derived from the Gibbs function:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \tag{12.6.12}$$

For the second term on the right hand side we obtain

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial H}\right)_P \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \Big/ \left(\frac{\partial H}{\partial S}\right)_P = \frac{C_P}{T}. \tag{12.6.13}$$

Thus, equation 12.7.9 becomes

$$-\frac{VdP}{T} = -\left(\frac{\partial V}{\partial T}\right)_P dP + \frac{C_P dT}{T}. \tag{12.6.14}$$

Multiply through by *T*, and divide by *dP*, taking the infinitesimal limit as *dP* → 0, recalling that we are dealing with an experiment in which the enthalpy is constant, and we arrive at

$$-V = -T\left(\frac{\partial V}{\partial T}\right)_P + C_P\left(\frac{\partial T}{\partial P}\right)_H, \tag{12.6.15}$$

from which we immediately obtain

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right], \tag{12.6.16}$$

quod erat demonstrandum.

12.7: The Thermodynamic Functions for an Ideal Gas

In this section I tabulate the changes in the thermodynamic functions for an ideal gas taken from one state to another.

One mole of an ideal gas going isothermally and reversibly from P_1V_1T to P_2V_2T or adiabatically and reversibly from $P_1V_1T_1$ to $P_2V_2T_2$.

	Isothermal	Adiabatic
Work done **by** gas	$RT \ln(V_2/V_1)$*	$\frac{P_1V_1-P_2V_2}{\gamma-1} = \frac{R(T_1-T_2)}{\gamma-1} = C_V\left(T_1-T_2\right)$
$U_2 - U_1$	0	$-\frac{P_1V_1-P_2V_2}{\gamma-1} = -\frac{R(T_1-T_2)}{\gamma-1} = -C_V\left(T_1-T_2\right)$
Heat absorbed **by** gas	$RT \ln(V_2/V_1)$	0
$S_2 - S_1$	$R \ln(V_2/V_1)$	0
$H_2 - H_1$	0	$-\frac{P_1V_1-P_2V_2}{1-1/\gamma} = -\frac{R(T_1-T_2)}{1-1/\gamma} = -C_P\left(T_1-T_2\right)$
$A_2 - A_1$	$-RT \ln(V_2/V_1)$	$-\frac{R(T_1-T_2)}{\gamma-1} - T_2S_2 + T_1S_1$
$G_2 - G_1$	$-RT \ln(V_2/V_1)$	$-\frac{R(T_1-T_2)}{1-1/\gamma} - T_2S_2 + T_1S_1$

*Note that for isothermal processes on an ideal gas, we can write $(V_2/V_1) = (P_1/P_2)$.

A difficulty will be noted in the entries for the increase in the Helmholtz and Gibbs functions for an adiabatic process, in that, in order to calculate ΔA or ΔG, it is apparently necessary to know S_1 and S_2, and not merely their difference. For the time being this is a difficulty to note on one's shirt-cuff, and perhaps return to it later.

12.8: The Thermodynamic Functions for Other Substances

Calculation of the change in the thermodynamic functions of any substance going reversibly from $P_1V_1T_1$ to $P_2V_2T_2$.

The first comforting thing to note is that *SUHAG* are all state functions, and therefore the change in their values is route-independent.

Entropy.

Entropy is a function of state (i.e. of *PVT*), but since *PVT* are related through the equation of state, it is necessary to specify only two of these quantities. Thus, for example if we express S as a function of T and P, infinitesimal increases in these will give rise to an infinitesimal increase in S given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{12.8.1}$$

Now $\left(\frac{\partial S}{\partial T}\right)_P$ is (for a reversible process) $\frac{C_P}{T}$ (see equation 12.7.5), and $\left(\frac{\partial S}{\partial P}\right)_T$ is (by a Maxwell relation) equal to $-\left(\frac{\partial V}{\partial T}\right)_P$. If we know C_P as a function of temperature, and, if we know the equation of state, we can now calculate

$$S_2 - S_1 = \int_{T_1}^{T_2} C_P \frac{dT}{T} - \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP \tag{12.8.2}$$

This will enable us to calculate the change in entropy of a substance provided that we know how the heat capacity varies with temperature and provided that we know the equation of state.

For an ideal gas $\left(\frac{\partial V}{\partial T}\right)_P = R/P$, and so we obtain, for an ideal gas

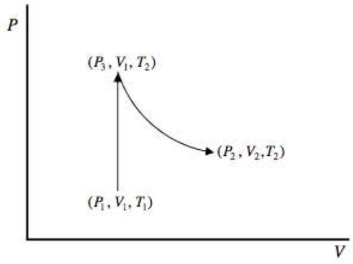
$$S_2 - S_1 = \int_{T_1}^{T_2} C_P \frac{dT}{T} - R\ln(P_2/P_1). \tag{12.8.3}$$

If we want to express the increase of entropy in terms of the change in temperature and volume, and of C_V, we can use $P_V = RT$ and $C_P = C_V + R$ to obtain

$$S_2 - S_1 = \int_{T_1}^{T_2} C_V \frac{dT}{T} + R\ln(V_2/V_1) \tag{12.8.4}$$

This agrees with what we had in the previous section for an isothermal expansion.

Here's another way or arriving at equation 12.9.4. We want to find the change in entropy of a mole of an ideal gas in going from (P_1, V_1, T_1) to (P_2, V_2, T_2). Since the change in entropy is route-independent, we can choose any simple route for which the calculation is easy. Let's go at constant volume from (P_1, V_1, T_1) to (P_3, V_1, T_2) and then at constant temperature from (P_3, V_1, T_2) to (P_2, V_2, T_2).



To go from (P_1, V_1, T_1) to (P_3, V_1, T_2), the gas has to absorb an amount of heat $\int_{T_1}^{T_2} C_V dT$, and so its entropy increases by $\int_{T_1}^{T_2} C_V \frac{dT}{T}$. To go from ($P_3$, V_1, T_2) to (P_2, V_2, T_2). The gas does work $RT_2 \ln(V_2/V_1)$ without any change in internal energy (because the internal energy of an ideal gas at constant temperature is independent of its volume), and therefore it absorbs this amount of heat. Therefore its entropy increases by $R\ln(V_2/V_1)$. Thus we arrive again at equation 12.9.4.

Example: If the substance is an ideal monatomic gas, then $C_P = \frac{5}{2}R$. From this we calculate

$$S_2 - S_1 = \frac{5}{2}R\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right) = R\ln\left[\left(\frac{T_2}{T_1}\right)^{5/2}\frac{P_1}{P_2}\right]. \tag{12.8.5}$$

Exercise: Go through the same analysis, but starting from $S = S(T, V)$. Show that the result you get for an ideal gas is the same as above. It will also, of course, necessarily be the same for any substance, though the equality of the expression you get with equation 12.9.2 may not be immediately apparent.

Exercise: The pressure and volume of an ideal monatomic gas are both doubled. What is the ratio of the new temperature to the old? What is the increase in the molar entropy?

(I make the answer 2.31×10^4 J kmole^{-1} K^{-1}.) Now try the same problem with an ideal diatomic gas. (I make the answer 3.46×10^4 J kmole^{-1} K^{-1}.)

Internal Energy and Enthalpy

These can be calculated if we know how C_V and C_P vary with temperature, because, by definition, $C_V = (\partial U/\partial T)_V$ and $C_P = (\partial H/\partial T)_P$.

Therefore

$$U_2 - U_1 = \int_{T_1}^{T_2} C_V dT \tag{12.8.6}$$

and

$$H_2 - H_1 = \int_{T_1}^{T_2} C_P dT. \tag{12.8.7}$$

Helmholtz and Gibbs Functions

Since $A = U - TS$, we have

$$A_2 - A_1 = U_2 - U_1 - T_2(S_2 - S_1) - S_1(T_2 - T_1). \tag{12.8.8}$$

In the special case of an ideal gas, we obtain

$$A_2 - A_1 = \int_{T_1}^{T_2} C_V dT - T_2\int_{T_1}^{T_2}\frac{C_V dT}{T} - RT_2\ln(V_2/V_1) - S_1(T_2 - T_1). \tag{12.8.9}$$

Since $G = H - TS$, we have

$$G_2 - G_1 = H_2 - H_1 - T_2(S_2 - S_1) - S_1(T_2 - T_1) \tag{12.8.10}$$

In the special case of an ideal gas, we obtain

$$G_2 - G_1 = \int_{T_1}^{T_2} C_p dT - T_2\int_{T_1}^{T_2}\frac{C_P dT}{T} - RT_2\ln(P_1/P_2) - S_1(T_2 - T_1). \tag{12.8.11}$$

There is, however, a serious difficulty with equations 12.9.9 and 12.9.11, in that, in order to calculate the change in the Helmholtz and Gibbs functions, we need to know the initial absolute entropy S_1.

12.9: Absolute Entropy

We can, of course, calculate the molar entropy of a substance at some temperature provided that we define the entropy at a temperature of absolute zero to be zero. By way of example, assuming that the molar entropy of hydrogen at 0 K is zero, calculate the absolute entropy of a kmole of H2 gas at a temperature of 25$^{\text{o}}$C (298.15 K) and a pressure of one atmosphere. We can do this in five stages, as follows. You will find it helpful to sketch these stages on a drawing similar to figure VI.5.

1. Heat the solid hydrogen from 0 K to 13.95 K at a pressure of 7173 Pa. (That’s the triple point.) The increase in entropy is $\int C_P\, d(\ln T)$. Assuming that we know C_P as a function of temperature in this range, that comes to 2080 J K^{-1} kmole^{-1}.

2. Liquefy it at the same temperature and pressure. The molar latent heat of fusion is 117000 J kmole^{-1}. Increase in entropy = 117000/13.95 = 8400 J K^{-1} kmole^{-1}.

3. Vaporize it at the same temperature and pressure. The molar latent heat of vaporization is 911000 kmole^{-1}. Increase in entropy = 911000/13.95 = 65300 J K^{-1} kmole^{-1}.

4. Increase temperature to 298.15 K at constant pressure. See equation 12.9.3. The increase in entropy is $\int C_P\, d(\ln T)$. Assuming that we know C_P as a function of temperature in this range, that comes to 70000 J K^{-1} kmole^{-1}.

5. Increase pressure to 1 atmos = 1.013 × 105 Pa at constant temperature. See equation 12.9.4, from which we see that there is a *decrease* of entropy equal to $R \ln(P_2/P_1) = 8314 \ln(1.103 \times 10^5 / 7173) = 22000$ J K^{-1} kmole^{-1}.

Hence, taking the entropy to be zero at 0 K, the required entropy is 124000 J K^{-1} kmole^{-1}.

Now that we have calculated the absolute entropy at a given temperature and pressure, we can calculate the increase in the Helmholtz and Gibbs functions from equations 12.9.9 and 12.9.11. But this leaves us in a rather uncomfortable position. After all, all we have done in this example is to calculate the *increase* in entropy as we took the sample up to 25 $^{\text{o}}$C and 1 atmosphere – we haven’t *really* calculated the *absolute* entropy. The entropy appearing in equations 12.9.9 and 12.9.11 is surely the *absolute* entropy, and we cannot calculate this unless we know the entropy at T = 0 K. This slight puzzle will remain with us until Chapter 16, when we meet Nernst’s Heat Theorem and the Third Law of Thermodynamics.

Many of the examples of thermodynamical calculations have hitherto involved *PdV* work in a system in which the working substance has been an ideal gas. Let us now look at two entirely different situations, both involving non-*PdV* work. Let us look at charging a battery, and creating new surface by distorting a spherical drop of liquid.

12.10: Charging a Battery

The concept of “non-*PdV* work” sometimes causes difficulty, so am going to illustrate it in this section by using the charging of a battery as an example, and in the next section by a discussion of surface tension. This section will also give us an opportunity of using a Gibbs-Helmholtz relation.

Suppose that we force a charge q into an electric cell whose electromotive force (EMF) is E, at constant temperature and pressure. What is the increase in the Gibbs function of the cell? And what is the increase in its enthalpy?

The answer to the first question is easy. It is just qE. The increase in the enthalpy is given by

$$\Delta H = \Delta G + T\Delta S$$

and, by a Maxwell relation (equation 12.6.12a), this is

$$\Delta H = \Delta G - T\Delta\left(\frac{\partial G}{\partial T}\right)_P, \tag{12.10.1}$$

which is one of the Gibbs-Helmholtz relations. But since ΔG = qE, this becomes

$$\Delta H = q\mathcal{E} - Tq\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P = q\left[\mathcal{E} - T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_P\right]. \tag{12.10.2}$$

Thus we can calculate the increase in enthalpy from a measurement of how the EMF of the cell changes with temperature.

12.11: Surface Energy

For a second example of non-*PdV* work we shall consider the phenomenon of "surface tension".

It is well known that a liquid tends to contract to a shape that minimizes its surface area. In the absence of other forces, this means that it will become spherical. The effect is often conveniently described in terms of "surface tension". We describe the tendency of a surface to contract by drawing an imaginary line in the surface, and we say that the surface to one side of the line pulls the surface of the other, and we call the force per unit length perpendicular to the line the *surface tension*. It is expressed in dynes per cm or newtons per metre. In this section I shall use the following symbols:

Surface tension: Γ

Area: σ

However, from the point of view of thermodynamics, it is easier to think of surface *energy*. How much *work* is needed to increase the surface area? And how is this related to what we have described as "surface tension"? It may be noted in passing that energy per unit area (J m^{-2}) is dimensionally similar to force per unit length (N m^{-1}).

A non-spherical blob of liquid will, under the action of surface tension, contract into a spherical blob – i.e. a blob of least surface area for a given volume. It should not come as a surprise to learn that, at least in principle, as the blob adjusts (in an adiabatic process) to its spherical shape of least surface area, it becomes warmer. Molecules near the surface have a high potential energy. As many of them fall beneath the surface as the surface area is decreased, this potential energy is converted to kinetic energy. Conversely, if a spherical drop is distorted from its spherical shape, it becomes cooler.

We have already pointed out that the surface tension can be regarded as the work required to create new area. Increasing the area will result in a fall in temperature, so, if the temperature is kept constant, some heat must be absorbed from the surroundings, and hence the increase in the internal energy is a little more than the surface tension. It may at first seem surprising that doing work on a liquid, in order to create new surface, results in a *fall* of temperature, but the work is being used not to increase the kinetic energy of the molecules, but rather to increase their potential energy by pulling them to the surface.

One way in which we can imagine work being done on a liquid to increase its surface area is simply to imagine distorting a spherical drop into a nonspherical shape. Another way, which might lend itself more easily to the sort of thermodynamical analysis we are accustomed to in discussing gases, is to imagine a film of soapy water held in a wire frame, constructed of a fixed U-shaped portion A (see figure XII.1), and a bridge B which we can move in and out, allowing us to do work on the liquid by pulling it to the right, or the liquid to do work by pulling the bridge to the left. We could even refer to these two parts as the "cylinder" A and the "piston" B. A difference between this picture and that of a gas inside a real cylinder is that when we pull the "piston" out, we are doing work on the liquid. Nevertheless, as explained above, the temperature of the liquid then drops. If we allow the film to contract and to pull the "piston" to the left, the temperature will rise.

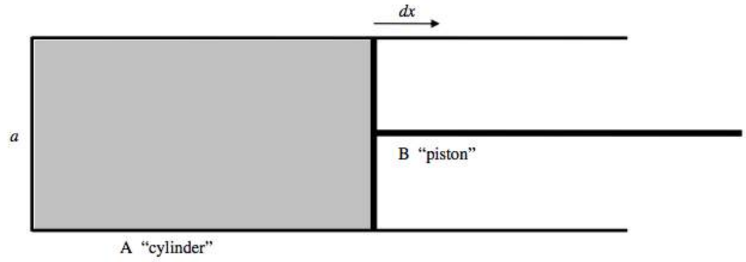


FIGURE XII.1

If the width of the "cylinder" is a, the surface tension force with which the liquid is pulling on the "piston" is $2a\Gamma$, where Γ is the surface tension. The factor 2 arises because there are two surfaces, above and below. If we pull the piston to the right through a distance dx, the work we do on the liquid is $2a\Gamma dx$. If we do this adiabatically (quickly), the liquid cools. If we do it isothermally (slowly), the liquid has to absorb some heat from its surroundings.

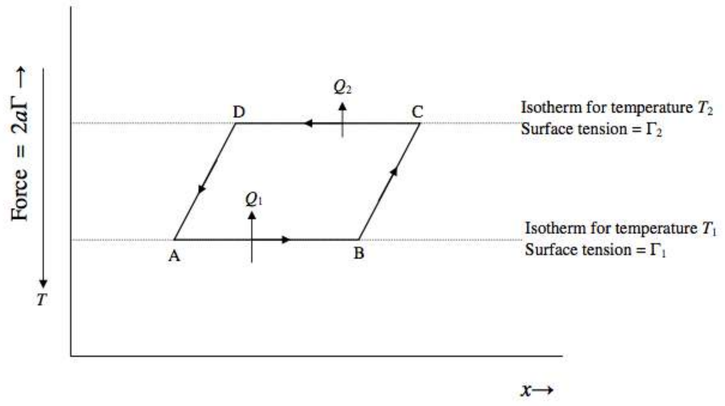


FIGURE XII.2

Let us now take the liquid around a Carnot cycle, as shown in figure XII.2. Notice that, as we move the "piston" to the right, provided that the temperature remains constant the surface tension force between the "piston" and the liquid does not change; thus the isotherms are horizontal lines, with the warmer isotherms lying lower than the cooler isotherms.

Let us start by moving the piston to the right, isothermally at a temperature T1, through a distance Δx, being the portion *AB* of figure XII.2. The work done on the liquid is $2a\Gamma_1\ \Delta x$, where Γ_1 is the surface tension at temperature T_1. In order that the process should be isothermal, the liquid has to absorb an amount of heat Q_1 from its surroundings. The internal energy increases by $2a\Gamma_1\Delta x + Q_1$.

Now expand the liquid further, but this time adiabatically, from B to C. Work is being done on the liquid, but no heat is being absorbed. The temperature drops to T_2. The new surface tension is Γ_2, which is greater than Γ_1, because surface tension generally decreases at warmer temperatures.

Now allow the liquid to contract isothermally at temperature T_2, from C to D. The liquid does an amount of work $2a\Gamma_2\Delta x$, and it must lose an amount of heat Q_2 (which, as we shall see, is less than Q_1) to its surroundings. The internal energy decreases by $2a\Gamma_2\Delta x + Q_2$.

Finally, return the liquid to its original state A along the adiabatic path DA. As many molecules on the surface fall back beneath the surface, the temperature rises to its original value T_1. Work is being done *by* the liquid; the work done *by* the liquid along DA is equal to the work done on it along BC.

The net work done *by* the liquid around the complete cycle is $2a(\Gamma_2 - \Gamma_1)\Delta x$ and the net heat absorbed by the liquid around the cycle is $Q_1 - Q_2$. Since there is no change in the internal energy around the cycle (because *U* is a function of state), these two are equal. Also, there is no change in entropy around the cycle (because S is a function of state), and therefore $Q_2/T_2 = Q_1/T_1$. (This justifies our earlier assertion that $Q_2 < Q_1$.)

From these two equations we obtain

$$\frac{Q_1}{T_1}(T_1 - T_2) = 2a(\Gamma_2 - \Gamma_1)\Delta x. \tag{12.11.1}$$

Go to the infinitesimal limit and drop the subscripts, and this becomes

$$Q = -T\frac{d\Gamma}{dT} \times 2a\Delta x. \tag{12.11.2}$$

The right hand side is a positive quantity, because $\frac{d\Gamma}{dT}$ is negative. We have seen that, in order to create new surface isothermally, heat must be absorbed. What equation 12.12.2 says is that the heat absorbed to create the new area $\Delta\sigma = 2a\Delta x$ created is equal to $Q = -T\frac{d\Gamma}{dT} \times \Delta\sigma$.

Now the *work required* to create the new area is $\Gamma \times \Delta\sigma$.

Thus the increase in internal energy when new area $d\sigma$ is created at constant temperature is

$$\Delta U = \left(\Gamma - T\frac{d\Gamma}{dT}\right)\Delta\sigma. \tag{12.11.3}$$

This will remind you of equation 12.11.1, $\Delta H = \Delta G - T\Delta\left(\frac{\partial G}{\partial T}\right)_P$, for the increase in enthalpy of a battery when we add charge to it at constant pressure. This time we are adding new area to a liquid at constant volume.

Here is *another* way at arriving at the same result: It will remind you of the way in which, in this Chapter, we derived the expression for the Joule coefficient.

The increase in internal energy and Helmholtz functions of a system when we add heat to it and do work on it is given by the familiar equations

$$dU = TdS - PdV + \sum XdY \tag{12.11.4}$$

and

$$dA = -SdT - PdV + \sum XdY. \tag{12.11.5}$$

We are most familiar with them when the term $\sum XdY$ is zero, but in this case we are dealing with a liquid at constant volume, and the one XdY term is $\Gamma d\sigma$, so that the equations become

$$dU = TdS + \Gamma d\sigma \tag{12.11.6}$$

and

$$dA = -SdT + \Gamma d\sigma. \tag{12.11.7}$$

Divide equation 12.12.6 by $d\sigma$ at constant temperature:

$$\left(\frac{\partial U}{\partial \sigma}\right)_T = T\left(\frac{\partial S}{\partial \sigma}\right)_T + \Gamma. \tag{12.11.8}$$

From equation 12.12.7 obtain a Maxwell relation:

$$\left(\frac{\partial S}{\partial \sigma}\right)_T = -\left(\frac{\partial \Gamma}{\partial T}\right)_\sigma, \tag{12.11.9}$$

except that Γ is in any case independent of σ, so the right hand term is actually a total derivative, $d\Gamma/dT$.

Substitute this into equation 12.12.8 and we have the same result as in our previous argument:

$$\left(\frac{\partial U}{\partial \sigma}\right)_T = \Gamma - T\frac{d\Gamma}{dT}. \tag{12.11.10}$$

In summary, the increase in internal energy in creating $d\sigma$ of new surface at constant temperature is the sum of the work required, $\Gamma d\sigma$, and the heat absorbed, $-T\frac{d\Gamma}{dT}d\sigma$.

Here's *yet another way* of getting there! It will remind you of the way in which we derived the expression for the Joule coefficient in Chapter 10. In general the internal energy of a drop of liquid depends on its volume, temperature and surface area:

$$U = U(V, T, \sigma). \tag{12.11.11}$$

However, let us ignore the very small change in energy resulting from the very small amount of PdV work that the drop would do if it expands a tiny bit as a result of temperature increase. We shall be concerned only with internal energy as a function of temperature and of surface tension (which may vary with temperature.) Thus, we'll assume

$$U = U(T, \sigma). \tag{12.11.12}$$

For infinitesimal increases in temperature and surface tension, the corresponding increase in the internal energy is

$$dU = \left(\frac{\partial U}{\partial T}\right)_\sigma dT + \left(\frac{\partial U}{\partial \sigma}\right)_T d\sigma. \tag{12.11.13}$$

The internal energy could increase by the addition of heat **to** the drop, dQ, plus work done **on** it, dW. The former is TdS, and the latter is $+\Gamma d\sigma$. Thus

$$dU = TdS + \Gamma d\sigma. \tag{12.11.14}$$

From these we obtain

$$dS = \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_\sigma dT + \left\{\left(\frac{\partial U}{\partial \sigma}\right)_T - \Gamma\right\} d\sigma\right]. \tag{12.11.15}$$

Since entropy is a function of state, dS is an exact differential, and therefore

$$\frac{1}{T}\frac{\partial}{\partial \sigma}\left(\frac{\partial U}{\partial T}\right)_\sigma = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial \sigma}\right)_T - \frac{\Gamma}{T}\right]. \tag{12.11.16}$$

$$\frac{1}{T}\frac{\partial^2 U}{\partial \sigma \partial T} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial \sigma}\right)_T + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial \sigma} + \frac{\Gamma}{T^2} - \frac{1}{T}\left(\frac{\partial \Gamma}{\partial T}\right)_\sigma. \tag{12.11.17}$$

Therefore

$$\left(\frac{\partial U}{\partial \sigma}\right)_T = \Gamma - T\left(\frac{\partial \Gamma}{\partial T}\right)_\sigma. \tag{12.11.18}$$

Again, we point out that Γ cannot in any case depend on σ, so that last derivative is really a total derivative, so that

$$\left(\frac{\partial U}{\partial \sigma}\right)_T = \Gamma - T\frac{d\Gamma}{dT} \tag{12.11.19}$$

Surface tension generally decreases with temperature, so this equation shows that the increase of internal energy at constant temperature per unit new area is a little greater than the surface tension, as expected.

Can we calculate the fall in temperature if new area is created adiabatically and reversibly (i.e. isentropically)? Yes, because equation 12.12.15 (with $dS = 0$) tells us that then

$$\left(\frac{\partial U}{\partial T}\right)_\sigma dT = -\left[\left(\frac{\partial U}{\partial \sigma}\right)_T - \Gamma\right] d\sigma. \tag{12.11.20}$$

On making use of equation 12.12.19, we obtain

$$\left(\frac{\partial U}{\partial T}\right)_\sigma dT = T\left(\frac{\partial \Gamma}{\partial T}\right)_\sigma d\sigma. \tag{12.11.21}$$

We are assuming that the volume is constant so that $\left(\frac{\partial U}{\partial T}\right)_0 = C_V$, and therefore the increase in temperature with area is

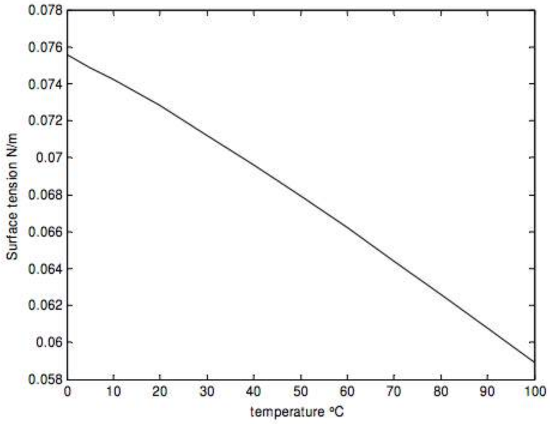
$$dT = \frac{T}{C_V}\left(\frac{\partial \Gamma}{\partial T}\right)_\sigma d\sigma = \frac{T}{C_V}\frac{d\Gamma}{dT} d\sigma. \tag{12.11.22}$$

Since $\frac{d\Gamma}{dT}$ is generally negative, this means that the temperature falls as the area is increased, as expected. In this equation, if $d\sigma$ means the increase in area of a sample, in m^2, then C_V means the heat capacity of that sample, in J K^{-1}.

Measurement of the surface tension of a liquid is very sensitive to how clean the surface is, but, for the record, the following figures for the surface tension of clean water in contact with air are taken from the Website www.engineeringtoolbox.com/watersurface-tension-d_597.html

Temperature - *t* - ($^{\text{o}}$C)	Surface Tension in contact with air - Γ - (N/m)
0	0.0756
5	0.0749
10	0.0742
20	0.0728
30	0.0712
40	0.0696
50	0.0679

60	0.0662
70	0.0644
80	0.0626
90	0.0608
100	0.0589



Exercise: A drop of water 1 mm in diameter at 45 °C is broken up into two equal droplets, each half the volume of the original drop. Calculate the change in temperature, and say whether it is cooler or warmer.

12.12: Fugacity

Problem: The pressure of a mole of an ideal gas is increased isothermally from P0 to P. What is the increase G − G0 in its Gibbs free energy?

Solution: By integration of equation 12.6.12b, $\left(\frac{\partial G}{\partial P}\right)_T = V$, or by use of $dG = -SdT + VdP$, we have

$$G - G_0 = \int_{P_0}^{P} VdP. \tag{12.12.1}$$

For a mole of an ideal gas, $V = RT/P$, and hence

$$G - G_0 = RT\ln(P/P_0), \tag{12.12.2}$$

which agrees with equation 12.9.11.

Equation 12.13.1 enables us to calculate the change in the Gibbs free energy of a substance while its pressure is increased at constant temperature. Equation 12.13.2 gives the result for a mole of an ideal gas. If the substance is not an ideal gas, then we need to know the equation of state, $V = V(P, T)$ in order to integrate equation 12.13.1. For example, the equation of state for a van der Waals gas is $\left(P + a/V^2\right)(V - b) = RT$, where V is the molar volume, or $PV^3 - (bP + RT)V^2 + aV - ab = 0$.

Integrating equation 12.13.1 with this van der Waals equation of state may appear formidable. I am grateful to Dr J. Visvanathan of Chennai, India, for pointing out that it is not necessary. Instead one can calculate the change in the Helmholtz function, which, at constant temperature, is given by $A - A_0 = -\int_{V_0}^{V} PdV$, which is easy, and then use $G - G_0 = A - A_0 + PV - P_0V_0$. I am also indebted to Dr Justin Albert for pointing out that this amounts to integrating $\int_{P_0}^{P} VdP$ by parts, even if you had never heard of the Helmholtz function!

The *fugacity* f of a substance is defined in such a manner that, if the molar Gibbs free energy increases from G_0 to G, the ratio of the new fugacity to the initial fugacity, f/f_0, is given by

$$G - G_0 = RT\ln(f/f_0) \tag{12.12.3}$$

.

In other words, for a real substance, we can use all (or at least most!) of the equations that we know for an ideal gas as long as we substitute fugacity for pressure.

That is,

$$f/f_0 = \exp\left(\frac{G - G_0}{RT}\right). \tag{12.12.4}$$

As for internal energy, only the *difference* between the Gibbs free energies of two states can be defined; likewise, only the *ratio* of the fugacities of two states is defined.

Combining equations 12.13.4 and 12.13.1 we obtain

$$\ln(f/f_0) = \frac{1}{RT}\int_{P_0}^{P} VdP, \tag{12.12.5}$$

which should enable us to find the relation between pressure and fugacity if we know the equation of state.

We note also that at very low pressures, a real gas behaves more and more like an ideal gas, and we can define the fugacity in units of pressure (pascal) in such a manner that, in the limit, as the pressure approaches zero, the fugacity equals the pressure. Indeed, we can then define the ratio of the fugacity to the pressure as the *activity coefficient*, which has the value unity at zero pressure.

Problem: Show that for a substance having the equation of state $P(V - b) = RT$ (V = molar volume), as the pressure increases from P0 to P, the ratio of the final to initial fugacities is

$$\ln(f/f_0) = \ln(P/P_0) + \frac{b(P - P_0)}{RT}. \tag{12.12.6}$$

That is,

$$\ln f - \ln f_0 = \ln P - \ln P_0 + \frac{b\,(P - P_0)}{RT}. \tag{12.12.7}$$

Now suppose that P0 is very small, and in the limit, as $P_0 \to 0$, $f_0 \to P_0$. We now find that the fugacity at temperature T and pressure P is given by

$$\ln f = \ln P + \frac{bP}{RT}. \tag{12.12.8}$$

This can be written

$$\frac{f}{P} = \exp\left(\frac{bP}{RT}\right). \tag{12.12.9}$$

The ratio *f/P* is called the activity coefficient. You can see that $f \approx P$ if P is small, or if b is small, as expected.

CHAPTER OVERVIEW

13: Expansion, Compression and the TdS Equations

Topic hierarchy

13.1: Coefficient of Expansion

Notation: In an ideal world, I'd use α, β, γ respectively for the coefficients of linear, area and volume expansion. Unfortunately we need γ for the ratio of heat capacities. Many people use β for volume expansion, so I'll follow that. What, then, to use for area expansion? I'll use *b*, so we now have α, *b*, β, which is very clumsy. However, we shall rarely need b, so maybe we can survive.

Coefficient of linear expansion: α

Coefficient of area expansion: *b*

Coefficient of volume expansion: β

For small ranges of temperature, the increases in length, area and volume with temperature can be represented by

$$l_2 = l_1 \left[1 + \widehat{\alpha} \left(T_2 - T_1\right)\right] \tag{13.1.1}$$

$$A_2 = A_1 \left[1 + \hat{b} \left(T_2 - T_1\right)\right] \tag{13.1.2}$$

and

$$V_2 = V_1 \left[1 + \widehat{\beta} \left(T_2 - T_1\right)\right] \tag{13.1.3}$$

Here $\hat{\alpha}$, $\hat{b}$ and $\widehat{\beta}$ are the approximate coefficients of linear, area and volume expansion respectively over the temperature range T_1 to T_2. For all three, the units are degree^{-1} – that is C^{o-1} or K^{-1}.

For anisotropic crystals, the coefficient may be different in different directions, but for isotropic materials we can write

$$A_2 = l_2^2 = l_1^2 \left[1 + \hat{\alpha} \left(T_2 - T_1\right)\right]^2 = A_1 \left[1 + 2\tilde{\alpha} \left(T_2 - T_1\right) + \ldots\right] \tag{13.1.4}$$

$$V_2 = l_2^3 = l_1^3 \left[1 + \hat{\alpha} \left(T_2 - T_1\right)\right]^3 = V_1 \left[1 + 3\tilde{\alpha} \left(T_2 - T_1\right) + \ldots\right] \tag{13.1.5}$$

Thus for small expansions, $\hat{b} \approx 2\tilde{\alpha}$ and $\widehat{\beta} \approx 3\hat{\alpha}$.

Equations 13.1.1, 2 and 3 define the approximate coefficients over a finite temperature range. *The* coefficients *at* a particular temperature are defined in terms of the derivatives, i.e.

$$\alpha = \frac{1}{l} \left(\frac{\partial l}{\partial T}\right)_P, \tag{13.1.6}$$

$$b = \frac{1}{A} \left(\frac{\partial A}{\partial T}\right)_P \tag{13.1.7}$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P. \tag{13.1.8}$$

The relations *b* = 2α and β = 3α are exact.

We specify "at constant pressure" because obviously we don't want, in our definition, to prevent the material from expanding by increasing the pressure on it when we heat it.

For solids, the coefficient of linear expansion is usually the appropriate parameter; for liquids and gases the volume coefficient is usually appropriate. For most familiar common metals the coefficient of linear expansion is of order 10^{-5} K^{-1}. Alloys such as the nickel-steel alloy, "invar", used in clock construction, may have much smaller coefficients. Ordinary glass has a coefficient only a little less than that of metals; pyrex and fused quartz have a much smaller expansion – hence their use in telescope mirrors. For liquids and gases it is usually the volume coefficient that is quoted. The volume coefficient of mercury is about 0.00018 K^{-1}. Water actually contracts between 0 and 4 ^{o}C, and expands above that temperature. The volume coefficient of air at 0 ^{o}C is 0.0037 K^{-1}.

At room temperatures and above, the coefficient of linear expansion of metals doesn't vary a huge amount with temperature, but at low temperatures the coefficient of expansion varies much more rapidly with temperature – and so does the specific heat capacity (see Section 8.10). Indeed, for a given metal, the variation of expansion coefficient and the specific heat capacity vary with temperature in a rather similar manner, so that, for a given metal, the ratio α/C_P is constant over a large temperature range.

Exercise: A square metal plate has a circular hole of area 300 cm^2 in the middle of it. If the coefficient of linear expansion is 2 × 10^{-5} C$^{\text{o}-1}$, calculate the area of the hole when the temperature of the plate is raised through 100 degrees.

Exercise: Show that the coefficient of volume expansion of an ideal gas is 1/*T*. Compare this with the numerical value for air given above.

Although classical thermodynamics does not deal with detailed microscopic processes, it is of interest to ask *why* a solid material expands upon heating. Let us imagine a crystalline solid to be made up of atoms connected to each other by little springs, and each spring is governed by Hooke's Law, and consequently each atom is vibrating in a parabolic potential well and is moving in simple harmonic motion. If we increase the temperature, we increase the *amplitude* of the vibrations, but we *do not change the mean positions of the atoms*. Consequently, in such a model, we would not expect any expansion upon heating. However, the real potential is not parabolic, but is shaped, at least qualitatively, something like the Lennard-Jones or Morse potentials mentioned in Chapter 6, Section 6.8. If the material is heated, the amplitude of the vibrations increases, and, because of the higher-order terms in the potential, which give the potential its asymmetric anharmonic shape, the mean separation of the atoms does indeed increase, and so we have expansion. Thus the expansion upon heating of a solid material is a consequence of the anharmonicity of the atomic vibrations and the asymmetry of the potential in which they are moving.

In the next two exercises, I shall be thinking of the expansion of a metal rod as the temperature is increased, and the pressure will be assumed to be constant at all times. Thus I am going to assume that pressure is not a variable in the discussion, and I shall define the coefficient of linear expansion as $\alpha = \frac{1}{l}\frac{dl}{dT}$ rather than the more general $\frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_P$. A small point that I make at this stage is this: Suppose that the length of a metal rod increases linearly with temperature, so that $\frac{dl}{dT}$ that this does *not* mean that the coefficient of expansion is independent of temperature. And if α *is* independent of temperature, *l* does *not* increase linearly with temperature. The next two exercises will illustrate that, and will also illustrate how the exact coefficient $\alpha = \frac{1}{l}\frac{dl}{dT}$ is related to what I have called (for want of a better term) the "approximate" coefficient $\widehat{\alpha} = \frac{1}{l_1}\frac{l_2-l_1}{T_2-T_1}$.

Exercise. Suppose that the length of a metal rod increases with temperature according to $l = l_0\left(1+\alpha_0 T\right)$ where l_0 is the length at 0 K, and α_0 is the coefficient at 0 K. This means that $\frac{dl}{dT}$ and $l\alpha$ are independent of temperature, and each is equal to $l_0\alpha_0$. Show that the coefficient at temperature *T* is given by

$$\alpha = \frac{\alpha_0}{1+\alpha_0 T}. \tag{13.1.9}$$

Show that $\widehat{\alpha}$, the approximate coefficient over the temperature range T_1 to T_2, is equal to the exact coefficient α evaluated at $T = T_1$.

Exercise. Suppose that the coefficient α is independent of temperature. Show that the length of the rod increases with temperature according to $l = l_0 e^{aT}$, where l_0 is the length at 0 K. Show also that $\hat{\alpha} = \frac{e^{\alpha(T_i - T_1)}-1}{T_2-T_1}$.

By this time, it may have occurred to the reader that what we have called α) , for all its usefulness in the equation $l_2 = l_1\left[1+\widehat{\alpha}\left(T_2-T_1\right)\right]$, is not "the" coefficient of expansion at temperature T_1, nor is it the mean coefficient in the temperature range T_1 to T_2. The *mean* coefficient in this range must be defined by $\overline{\alpha}\left(T_2-T_1\right) = \int_{T_1}^{T_2}\alpha dT$. So now, one more exercise:

Exercise. Suppose that the length of a metal rod increases with temperature according to $l = l_0\left(1+\alpha_0 T\right)$, where l_0 is the length at 0 K, and α_0 is the coefficient at 0 K. Show that

$$\overline{\alpha} = \frac{1}{\left(T_2-T_1\right)}\ln\left(\frac{1+\alpha_0 T_2}{1+\alpha_0 T_1}\right). \tag{13.1.10}$$

Summary

If $\frac{dl}{dT}$ is constant	If α is constant
$l = l_0\left(1+\alpha_0 T\right)$	$l = l_0 e^{\alpha T}$
$\alpha = \frac{\alpha_0}{1+\alpha_0 T}$	$\alpha = \alpha_0$
$\widehat{\alpha} = \alpha_1$	$\widehat{\alpha} = \frac{e^{\alpha\left(T_i - T\right)}-1}{T_2-T_1}$
$\overline{\alpha} = \frac{1}{\left(T_2-T_1\right)}\ln\left(\frac{1+\alpha_0 T_2}{1+\alpha_0 T_1}\right)$	$\overline{\alpha} = \alpha$

(13.1.11)

Of course, you may feel that this distinction between $\alpha, \alpha_0, \hat{\alpha}$ and $\overline{\alpha}$ is splitting hairs. Let us discover for ourselves how much they differ, by putting in some numbers. Let us suppose that $\alpha_0 = 1.7 \times 10^{-5}\ \mathrm{K}^{-1}$ and that $l_0 = 1$ m. Then, assuming that $T_1 = 280$ K (6.85 °C) and $T_2 = 380$ K (106.85 °C), we obtain

$$\begin{array}{ll} \text{If } \frac{dl}{dt} \text{ is constant} & \text{If } \alpha \text{ is constant} \\ l_1 = 1.004760\mathrm{m} & 1.004771\mathrm{m} \\ \alpha(280\mathrm{K}) = 1.691946 \times 10^{-5}\mathrm{K}^{-1} & \alpha(280\mathrm{K}) = 1.700000 \times 0^{-5}\mathrm{K}^{-1} \\ \widehat{\alpha} = 1.691946 \times 10^{-5}\mathrm{K}^{-1} & \hat{\alpha} = 1.701446 \times 10^{-5}\mathrm{K}^{-1} \\ \overline{\alpha} = 1.690516 \times 10^{-5}\mathrm{K}^{-1} & \overline{\alpha} = 1.700000 \times 0^{-5}\mathrm{K}^{-1} \end{array}$$

In general, if the length at T_1 is l_1, the length l_2 at T_2 will be given by

$$l_2 = l_1 \exp\left(\int_{T_1}^{T_2} \alpha dT\right). \tag{13.1.12}$$

In the case where dl/dT is constant, so that $\alpha = \frac{\alpha_0}{1+\alpha_0 T}$, this becomes

$$l_2 = l_1 \left(\frac{1+\alpha_0 T_2}{1+\alpha_0 T_1}\right) = l_1 \left(1+\alpha_0 (T_2 - T_1) - \alpha_0^2 T_1 (T_2 - T_1) + \ldots\right). \tag{13.1.13}$$

In the case where α is constant, so it becomes

$$l_2 = l_1 \exp(\alpha (T_2 - T_1)) = l_1 \left(1 + \alpha (T_2 - T_1) + \frac{1}{2}\alpha^2 (T_2 - T_1)^2 + \ldots\right) \tag{13.1.14}$$

Thus to the first order of small quantities, all varieties of α are equal.

Coefficient of Expansion as a Tensor Quantity. In Chapter 4, I briefly mentioned that, in the case of an anistropic crystal, the coefficient of thermal conduction is a tensor quantity. The same is true, for an anisotropic crystal, of the coefficient of expansion. Thus, if, during an physics examination, you were asked to give examples of tensor quantities, you could give these as examples – though a small risk might be involved if your teacher had not thought of these as tensors! The coefficient of expansion of an anisotropic crystal may vary in different directions. (In Iceland Spar – calcium carbonate – in one direction the coefficient is actually negative.) If you cut an anisotropic crystal in the form of a cube, whose edges are not parallel to the crystallographic axis, the sample, upon heating, will not only expand in volume, but it will change in shape to become a non-rectangular parallelepiped. However, it is possible to cut the crystal in the form of a cube such that, upon heating, the sample expands to a rectangular parallelepiped. The edges of the cube (and the resulting parallelepiped) are then parallel to the *principal axes of expansion*, and the coefficients in these directions are the *principal coefficients of expansion*. These directions will be parallel to the crystallographic axes if the crystal has one of more axes of symmetry (but obviously not otherwise)

13.2: Compression

The way in which the volume of a material decreases with pressure at constant temperature is described by the *isothermal compressibility*, κ:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T. \tag{13.2.1}$$

Note the necessary minus sign.

Later, we shall need to distinguish between "isothermal compressibility" and "adiabatic compressibility", and we shall need a subscript to the symbol κ in order to distinguish between the two. For the time being, however, κ with no subscript will be taken to mean the isothermal compressibility.

The reciprocal of κ is called the isothermal *bulk modulus*, sometimes (understandably) called the isothermal *incompressibility*.

Question: What are the SI units for compressibility and bulk modulus?

Exercise: Show that the isothermal compressibility of an ideal gas is $1/P$.

Exercise: What is the bulk modulus of air at atmospheric pressure?

13.3: Pressure and Temperature

The way in which the pressure of a material increases with temperature at constant volume is described by $\left(\frac{\partial P}{\partial T}\right)_V$.

Exercise: By making use of equation 2.4.11, show that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}. \tag{13.3.1}$$

Exercise: By making use of equation 10.4.8, show that

$$C_P - C_V = \frac{TV\beta^2}{\kappa} = \frac{9TV\alpha^2}{\kappa}. \tag{13.3.2}$$

Thus we can determine $C_P - C_V$ from measurements of the expansion coefficient and the isothermal compressibility without knowing the equation of state. We have already shown that the expansion coefficient of an ideal gas is $1/T$, and the isothermal compressibility of an ideal gas is $1/P$. Note that, for an ideal gas, $\beta = 1/T$ and $\kappa = 1/P$, so that equation 13.3.2 reduces to R.

Note that, in equation 13.3.2, κ is the isothermal compressibility. C_P and C_V may denote the molar heat capacities (in which case V is the molar volume); or they may denote the specific heat capacities (in which case V is the specific volume or reciprocal of density); or they may denote the total heat capacities (in which case V is the total volume).

Recall that the physical reason that C_P is greater than C_V is that when a substance is heated and expands at constant pressure, it does work, whereas if held at constant volume it does no work. In the case of an ideal gas expanding reversibly, the work done is all external work. A real gas, or a van der Waals gas, on expanding also does internal work against the intermolecular forces. Therefore C_P is greater than C_V by more than R − but only a little more, because the intermolecular (van der Waals) forces are not very large. In Chapter 10 we developed an explicit expression for $C_P - C_V$ for a van der Waals gas (equation 10.4.10). When a solid is heated, it expands very little compared with a gas, and hence does very little external work. The intermolecular forces, however, are quite large, and hence an expanding solid does quite a lot of internal work. Thus for a gas, most of the work of expansion is external; for a solid, most of the work of expansion is internal.

Here are order-of-magnitude figures for copper at room temperature (for exact figures, we would have to specify the exact temperature).

Specific heat capacity at constant pressure = 384 J K^{-1} kg^{-1}

Molar mass ("atomic weight") = 63.5 kg kmole^{-1}

Molar heat capacity at constant pressure = 24400 J K^{-1} kmole^{-1} = 2.93 R.

Density = 8960 kg m^{-3}

Molar volume = 7.09×10^{-3} m^3 kmole^{-1}

Coefficient of linear expansion = 1.67×10^{-5} K^{-1}

Coefficient of volume expansion = 5.00×10^{-5} K^{-1}

Isothermal bulk modulus = 1.40×10^{11} Pa

Isothermal compressibility = 7.14×10^{-12} Pa^{-1}

Equation 13.3.2 will give us, at a temperature of 20 °C = 293.15 K, $C_P - C_V$ (molar) = 728 J K^{-1} kmole^{-1} = 0.09R. $C_P - C_V$ (specific) = 11 J K^{-1} kg^{-1} This is only about 3 percent of C_P.

Equation 13.3.2 raises an interesting problem concerning water. It will be understood that the reason why C_P for an ideal gas is greater than C_V is as follows. When heat is added to an ideal gas at constant volume, all of the heat goes into raising the temperature. When heat is added at constant pressure, however, some of the heat goes into doing external work. Hence $C_P > C_V$. That argument is correct. However...

Water at 2 ºC (or indeed at any temperature in the range between 0 ºC and 4 ºC) contracts upon heating (i.e. β is negative), so that, if we add heat at constant pressure, work is done on the water by its surroundings, and hence (we might argue, though erroneously), for water at 2 ºC, $C_P < C_V$. Equation 13.3.2, however, shows that $C_P \geq C_V$ regardless of the sign of β. (The equality applies where β = 0, which occurs at 4 ºC.) Thus we have a paradox.

In fact, equation 13.3.2 is correct, and, at 2 ºC, . $C_P > C_V$. The explanation is as follows. It is true that, when heat is added to an ideal gas at constant volume, all of the heat goes into raising the temperature – but this is true only for an ideal gas in which the internal energy is all kinetic. But for real substances, including water, the correct statement (which is really just the first law of thermodynamics) is that when heat is added to a substance at constant volume, all of the heat goes into raising the *internal energy*, and, for a nonideal substance the internal energy is partly kinetic and partly potential. When we add heat isobarically to water at 2 ºC, more of this heat goes into increasing the potential energy than if we add heat isochorically, and hence C_P is still greater than C_V. A very clear account of this problem, from both the thermodynamical and statistical mechanical points of view, is to be found in a paper by McDougall and Feistel, *Deep-Sea Research I* **50**, 1523 (2003).

(You may remember a similar apparent paradox in connection with surface tension of a liquid. When we do work adiabatically and reversibly to create new surface, the temperature *drops*. So doing work on a system or adding heat to it doesn't necessarily result in a rise in temperature. It *does* result in an increase of internal energy, which include potential energy.)

13.4: The TdS Equations

The three *TdS* equations have been known to generations of students as the “tedious equations” − though they are not at all tedious to a true lover of thermodynamics, because, among other things, they *enable us to calculate the change of entropy* during various reversible processes in terms of either *dV* and *dT*, or *dP* and *dT*, or *dV* and *dP*, and even in terms of directly measurable quantities such as the coefficient of expansion and the bulk modulus.

i.) We can express entropy in terms of any two of *PVT*. Let us first express entropy as a function of *V* and *T*

$$dS=\left(\frac{\partial S}{\partial V}\right)_T dV+\left(\frac{\partial S}{\partial T}\right)_V dT. \tag{13.4.1}$$

Therefore

$$TdS=T\left(\frac{\partial S}{\partial V}\right)_T dV+T\left(\frac{\partial S}{\partial T}\right)_V dT. \tag{13.4.2}$$

From a Maxwell relation (equation 12.6.15), $\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial P}{\partial T}\right)_V$. Also, in a constant volume process, *TdS* = *dU* so that $T\left(\frac{\partial S}{\partial T}\right)_V=\left(\frac{\partial U}{\partial T}\right)_V=C_V$.

Therefore $TdS=T\left(\frac{\partial P}{\partial T}\right)_V dV+C_V dT$.

This is the first of the *TdS* equations.

ii.) This time, let us express entropy as a function of *P* and *T*

$$dS=\left(\frac{\partial S}{\partial P}\right)_T dP+\left(\frac{\partial S}{\partial T}\right)_P dT. \tag{13.4.3}$$

Therefore

$$TdS=T\left(\frac{\partial S}{\partial P}\right)_T dP+T\left(\frac{\partial S}{\partial T}\right)_P dT. \tag{13.4.4}$$

From a Maxwell relation (equation 12.6.16), $\left(\frac{\partial S}{\partial P}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_P$. Also, in a constant pressure process, *TdS* = *dH* so that $T\left(\frac{\partial S}{\partial T}\right)_P=\left(\frac{\partial H}{\partial T}\right)_P=C_P$.

Therefore

$$TdS=-T\left(\frac{\partial V}{\partial T}\right)_P dP+C_P dT. \tag{13.4.5}$$

This is the second of the *TdS* equations.

iii.) If we express entropy as a function of *P* and *V* (recall that we can choose to express a function of state as a function of any two of *P*, *V* or *T*) we have

$$dS=\left(\frac{\partial S}{\partial P}\right)_V dP+\left(\frac{\partial S}{\partial V}\right)_P dV. \tag{13.4.6}$$

Therefore

$$TdS=T\left(\frac{\partial S}{\partial P}\right)_V dP+T\left(\frac{\partial S}{\partial V}\right)_P dV. \tag{13.4.7}$$

In a constant volume process, *TdS* = *CVdT*, so that $T\left(\frac{\partial S}{\partial P}\right)_V=C_V\left(\frac{\partial T}{\partial P}\right)_V$.

And in a constant pressure process, *TdS* = *CPdT*, so that

$$T\left(\frac{\partial S}{\partial V}\right)_p = C_P\left(\frac{\partial T}{\partial V}\right)_P. \tag{13.4.8}$$

Therefore

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV. \tag{13.4.9}$$

This is the third of the TdS equations.

In summary, then, these are the three *TdS* equations:

$$TdS = T\left(\frac{\partial P}{\partial T}\right)_V dV + C_V dT \tag{13.4.10}$$

$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP + C_P dT \tag{13.4.11}$$

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV \tag{13.4.12}$$

These equations can be used, for example, to calculate, by integration, the change of entropy between one state and another, provided that the equation of state is known in order that we can evaluate the partial derivatives.

13.5: Expansion, Compression and the TdS Equations

It will be recalled, from equations 13.3.1 and 13.1.8, that

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{\beta}{\kappa} \quad \text{and} \quad \left(\frac{\partial V}{\partial T}\right)_P=\beta V. \tag{13.5.1}$$

That is,

$$\left(\frac{\partial T}{\partial P}\right)_V=\frac{\kappa}{\beta} \quad \text{and} \quad \left(\frac{\partial T}{\partial V}\right)_P=\frac{1}{\beta V}. \tag{13.5.2}$$

With these, the TdS equations become

$$dS=\frac{\beta}{\kappa}dV+\frac{C_V}{T}dT \tag{13.5.3}$$

$$dS=-\beta V dP+\frac{C_p}{T}dT \tag{13.5.4}$$

and

$$dS=\frac{C_V\kappa}{T\beta}dP+\frac{C_P}{T\beta V}dV \tag{13.5.5}$$

These equations can be used, for example, to calculate, by integration, the change of entropy between one state and another, provided that β, κ and the heat capacities are known as functions of temperature and pressure or specific volume. You don't even have to know the equation of state.

They won't tell us anything about an ideal gas that we don't already know, but let's just apply them to an ideal gas in any case, just to see if we have made any mistakes so far. For an ideal gas, as we saw in Sections 13.1 and 13.2, $\beta = 1/T$ and $\kappa = 1/P$. The first two *TdS* equations become

$$TdS=PdV+C_VdT \tag{13.5.6}$$

and

$$TdS=-VdP+C_PdT. \tag{13.5.7}$$

That is to say,

$$TdS=PdV+dU \tag{13.5.8}$$

and

$$TdS=-VdP+dH \tag{13.5.9}$$

so all is well with the world so far. The third equation becomes

$$dS=C_V\frac{dP}{P}+C_P\frac{dV}{V}. \tag{13.5.10}$$

For a reversible adiabatic process, $dS = 0$, so what do you get if you integrate equation 13.5.10 for a reversible adiabatic process for an ideal gas? This should complete your happiness – though there is more to come.

If a material (be it solid, liquid or gas) is compressed reversibly and *adiabatically* (i.e. $dS = 0$), equation 13.5.3 **will tell you how the temperature changes with volume**:

$$\left(\frac{\partial T}{\partial V}\right)_S=-\frac{\beta T}{\kappa C_V}. \tag{13.5.11}$$

If it is the pressure, rather than the volume, that is changed reversibly and *adiabatically*, equation 13.5.4 **will tell you how the temperature changes with pressure**:

$$\left(\frac{\partial T}{\partial P}\right)_S = +\frac{\beta VT}{C_P}. \tag{13.5.12}$$

In equation 13.5.11, κ is the isothermal compressibility, defined in equation 13.2.1 as $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. To emphasize that this is the *isothermal* compressibility, I'll add a subscript: κ_{iso}. There is also a need to define an *adiabatic* compressibility, $\kappa_{\text{ad}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$. (Note - I used the word adiabatic, but I used the subscript S to the partial derivative. Are the words *adiabatic* and *isentropic* synonymous?) This is going to be less that the isothermal compressibility, because, if you try to compress a material adiabatically it will become hot and therefore not be as readily compressible as if the compression were isothermal. Now refer to equation 13.5.5, $dS = \frac{C_V\kappa_{\text{iso}}}{T\beta}dP + \frac{C_P}{T\beta V}dV$. Divide both sides by dP and go to the infinitesimal limit, recalling that in a reversible adiabatic process S is constant, and this equation then gives us $C_V\kappa_{iso} = -C_P.\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$. But $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ is the adiabatic compressibility, and C_P/C_V = γ, CP CV so we arrive at

$$\frac{\kappa_{\text{iso}}}{\kappa_{\text{ad}}} = \gamma, \tag{13.5.13}$$

where γ is the ratio of the isobaric and isochoric heat capacities. In particular, recall that, for an ideal gas, $\kappa_{\text{iso}} = 1/P$. Hence, for an ideal gas, $\kappa_{\text{ad}} = 1/(\gamma P)$.

In equation 13.3.2, we deduced the relation $C_P - C_V = \frac{TV\beta^2}{\kappa_{\text{iso}}}$. In equation 13.5.13, we have deduced an expression for the ratio of the isothermal to adiabatic compressibilities, the isothermal compressibility being greater. Combining these now with $\gamma = C_P/C_V$, we can now deduce an expression for the difference between the isothermal and adiabatic compressibilities, namely:

$$\kappa_{\text{iso}} - \kappa_{\text{ad}} = \frac{TV\beta^2}{C_P}. \tag{13.5.14}$$

In terms of *bulk modulus B*, which is the reciprocal of compressibility, equations 13.5.13 and 13.5.14 are, of course, $\frac{B_{\text{ad}}}{B_{\text{iso}}} = \gamma$ and $\frac{1}{B_{\text{iso}}} - \frac{1}{B_{\text{ad}}} = \frac{TV\beta^2}{C_P}$.

Comparison of equations 13.3.2 and 13.5 14 shows that

$$\frac{C_P}{C_V} = \frac{\kappa_{\text{iso}}}{\kappa_{\text{ad}}}. \tag{13.5.15}$$

Sir Isaac Newton in his Principia correctly deduced that the speed of sound in a gas is equal to $\sqrt{1/(\rho\kappa)}$, where ρ is the density, and without making any distinction between κ_{iso} and κ_{ad}. The measured speed was faster than predicted from his theory, and Newton tried, not completely successfully, to account for the difference. I haven't gone into the history, but there is a story – probably apocryphal – that, in order to secure agreement between observation and theory, he "fudged his lab" and "adjusted" his experimental results a little. But the trouble was not with the experimental results. If you take for κ the isothermal value, namely $1/P$ for an ideal gas (to which air approximates quite well over the small pressure changes involved), the theory gives $\sqrt{P/\rho}$ for the sound speed. In fact, however, the compressions and rarefactions in a sound wave are so rapid that they are, in effect, adiabatic, so that it is the adiabatic compressibility κ_{ad} that should be used, giving $\sqrt{\gamma P/\rho}$ as the theoretical expression, which agrees well with the observed speed.

13.6: Young's Modulus

This Section is under revision.

13.7: Rigidity Modulus (Shear Modulus)

When we are discussing the bulk modulus of a material we are usually thinking in terms of applying pressure and noting the compression, so the adiabatic bulk modulus is usually greater than the isothermal bulk modulus. We could in principle also imagine a situation in which we are moving a material into a vacuum, thus decreasing the external pressure, and then measuring the resulting expansion. In that case we would find that the adiabatic bulk modulus is less than the isothermal bulk modulus – but that is a rather artificial situation. In Section 13.5 we derived (see equation 13.5.14) the usual relation for compression:

$$\frac{1}{B_{\text{iso}}}-\frac{1}{B_{\text{ad}}}=\frac{\beta^2 T}{\rho C_P}, \tag{13.7.1}$$

in which β is the volume coefficient of expansion, and C_P is the specific heat capacity at constant pressure. (Compare this with equations 13.6.12 and 13.6.20.)

We now must ask ourselves what is the difference between the adiabatic and isothermal rigidity moduli (also known as shear modulus). If you are unfamiliar with the rigidity modulus, see my Classical Mechanics notes, Chapter 20, Section 20.3.

The rigidity modulus involves no change in volume or length, and hence *there is no difference between the adiabatic and isothermal rigidity moduli*.

13.8: Volume, Temperature and the Grüneisen Parameter

If you compress a material adiabatically and reversibly (i.e. isentropically) its temperature goes up. The amount by which it goes up can be represented by the partial derivative $\left(\frac{\partial T}{\partial V}\right)_S$. Here, V could mean the total volume , the specific volume or the molar volume, according to context, and you would have to specify your units accordingly. The derivative is negative, because the temperature goes up as the volume is decreased.

[Compare this with the definition of the volume coefficient of expansion $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, which is positive. Think about the difference.]

A dimensionless version which also expresses the variation of temperature with volume would be $\frac{V}{T}\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial \ln T}{\partial \ln V}\right)_S$, and here there is no need to specify whether V means total, specific or molar. The derivative could also be written as $-\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S$, where ρ is the density. The positive value, $-\left(\frac{\partial \ln T}{\partial \ln V}\right)_S = +\left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S$ is called the *Grüneisen parameter*. We have already used the symbols G, g, Γ and γ for various things in these notes, so I am stuck for a suitable symbol. Sometimes non-italic symbols are used for dimensionless parameters, such as R for Reynolds number in aerodynamics. Let's try Gr for the Grüneisen parameter.

For an *ideal gas*, the relation between volume and temperature in a reversible adiabatic expansion is $TV^{\gamma-1}$ = constant, and therefore the Grüneisen parameter for an ideal gas is $\gamma - 1$.

In thinking about volume and temperature changes, we often have some sort of a gas (ideal or otherwise) in mind. However, geophysicists have to deal with very large pressures in the interior of the Earth, where volume and temperature changes of solids under pressure are not negligible, and geophysicists often make use of the Grüneisen parameter for solid materials.

For a bit of practice in deriving relationships between some of the quantities described in this chapter, see if you can show that

$$\mathrm{Gr} = \frac{\beta}{\rho C_V \kappa_{\mathrm{iso}}} = \frac{\beta}{\rho C_P \kappa_{\mathrm{ad}}} \tag{13.8.1}$$

and

$$\gamma = 1 + \mathrm{Gr}\,\beta T. \tag{13.8.2}$$

If ρ in these questions stands for density (mass per unit volume), what, precisely, are C_V and C_P? Total, specific or molar? Or does it not matter? What do these equations become in the case of an ideal gas?

14: The Clausius-Clapeyron Equation

Before starting this chapter, it would probably be a good idea to re-read Sections 9.2 and 9.3 of Chapter 9.

The Clausius-Clapeyron equation relates the latent heat (heat of transformation) of vaporization or condensation to the rate of change of vapour pressure with temperature. Or, in the case of a solid-liquid transformation, it relates the latent heat of fusion or solidification to the rate of change of melting point with pressure.

Let us imagine a vapour in equilibrium with its liquid held in a cylinder by a piston, at a constant temperature – namely the temperature at which the liquid and vapour are in equilibrium − that is to say, the boiling (or condensation) point for that pressure. We imagine the piston to be pulled out, at constant temperature; liquid evaporates and the pressure remains constant. If the piston is pushed in, vapour condenses, at constant temperature and pressure. During this process the pressure and temperature remain constant, so the *Gibbs free energy* of the *system* is constant.

Let G_1 be the specific Gibbs free energy for the *liquid*

and G_2 be the specific Gibbs free energy for the *vapour*.

Suppose that a mass *dm* of the liquid vaporizes, so that the Gibbs free energy for the liquid decreases by G_1dm and the Gibbs free energy for the vapour increases by G_2dm. But the Gibbs free energy for the system is constant. This therefore shows that, when we have a liquid in equilibrium with its vapour (i.e. at its boiling point) the *specific Gibbs free energies of liquid and vapour are equal*. (The same is true, of course, for the *molar* Gibbs free energies.) That is:

$$H_1 - TS_1 = H_2 - TS_2 \tag{14.1}$$

or

$$T(S_2 - S_1) = H_2 - H_1, \tag{14.2}$$

in which the enthalpy and entropy are *specific*. The left hand side is the specific latent heat of vaporization, and we already knew from Chapter 9 that this was equal to the difference in the specific enthalpies of liquid and vapour.

The equality of the specific Gibbs free energies of liquid and vapour can also be written

$$U_1 - TS_1 + PV_1 = U_2 - TS_2 + PV_2, \tag{14.3}$$

or

$$T(S_2 - S_1) = (U_2 - U_1) + P(V_2 - V_1). \tag{14.4}$$

This shows that the latent heat of vaporization goes into two things: To increase the internal energy upon vaporization (especially the increase of potential energy as the molecules are pulled apart from each other) and the PdV work done against the external pressure as the volume increases. Thus we could divide the latent heat into an internal latent heat and an external latent heat.

In the foregoing, we imagined that some liquid vaporized as we withdrew the piston. Now let us imagine that we cause some liquid to vaporize as we add some heat at constant volume. The specific Gibbs free energies of liquid and vapour both increase, but they increase by the same amount because, as we have seen, when a liquid and its vapour are in equilibrium at the boiling point, their specific Gibbs free energies are equal. Thus

$$-S_1dT + V_1dP = -S_2dT + V_2dP, \tag{14.5}$$

or

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1}. \tag{14.6}$$

The left hand side is the rate of increase of vapour pressure with temperature, while $S_2 - S_1$ is equal to L/T, where L is the specific latent heat of vaporization. Thus we arrive at the *Clausius-Clapeyron equation*:

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_\mathrm{L})}. \tag{14.7}$$

Example: At 100 $^\mathrm{o}$C the rate of increase of vapour pressure of steam is 27.1 mm Hg per Celsius degree, and a gram of steam occupies 1674 cm^3. What is the specific latent heat of vaporization?

Answer: $L = T\left(V_2 - V_1\right)\frac{dP}{dT}$.

$T = 373.15\mathrm{K}. \quad V_2 - V_1 = 1.673\mathrm{m}^3\mathrm{kg}^{-1}$.

$\frac{dP}{dT} = 1.36 \times 10^4 \times 9.81 \times 2.71 \times 10^{-2} = 3.616\mathrm{PaK}^{-1}$.

Hence

$$\underline{\underline{L = 2.26 \times 10^6\mathrm{Jkg}^{-1}}}.$$

The same argument can be used to relate the rate of change of melting point with pressure of a solid with its latent heat of fusion. The Clausius-Clapeyron equation then takes the form

$$\frac{dT}{dP} = \frac{T\left(V_2 - V_1\right)}{L}. \tag{14.8}$$

For most substances, the specific volume of the liquid (V_2) is greater than the specific volume of the solid (V_1); but for H_2O, Bi and Ga, $V_2 < V_1$ and dT/dP is negative.

Example: For the ice-water system,

$$\begin{aligned}&L = 3.36 \times 10^5\mathrm{Jkg}^{-1}\\&V_2 = 10^{-3}\mathrm{m}^3\mathrm{kg}^{-1}\\&V_1 = 1.091 \times 10^{-3}\mathrm{m}^3\mathrm{kg}^{-1}\\&T = 273.15\mathrm{K}\end{aligned}$$

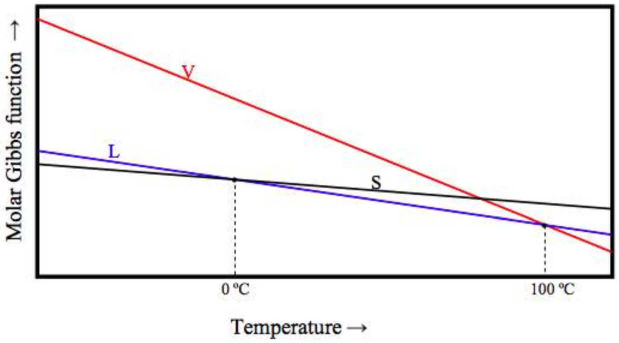
Hence

$$\frac{dT}{dP} = -7.4 \times 10^{-8}\mathrm{KPa}^{-1}$$

That’s about -7.4×10^{-3} kelvins per atmosphere

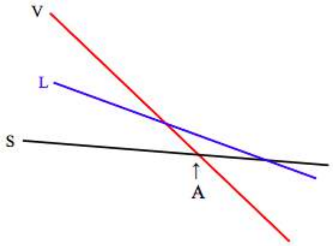
Solids, Liquids, Gases, Entropy and the Gibbs Function.

Of the three phases, solid, liquid and vapour, solid is the most ordered (has the least entropy) and vapour is the most disordered (has the most entropy). Now equation 12.6.12a tells us that $(\partial G/\partial T) = -S$. This means that, at a given pressure, the Gibbs function of the vapour decreases rapidly with increasing temperature, whereas the Gibbs function of a solid decreases relatively slowly. Schematically the Gibbs function of the three phases for H_2O at atmospheric pressure looks something like this:



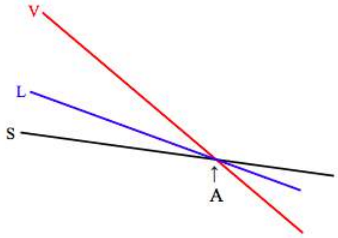
Below 0 ºC, the Gibbs function is lowest for the solid, and that is the stable phase. Between 0 ºC and 100 ºC, the Gibbs function is lowest for the liquid, and that is the stable phase. Above 100 ºC, the Gibbs function is lowest for the vapour, and that is the stable phase. At 0 ºC, the molar Gibbs function of solid and liquid are equal; the two phases there are in equilibrium. At 100 ºC, the molar Gibbs function of gas and liquid are equal; the two phases there are in equilibrium.

The slopes and intercepts of these lines vary not only from substance to substance, but also, for a given substance, with pressure. The Maxwell relation 12.6.16, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, tells us that the manner in which entropy changes with pressure is related to the expansion coefficient. For most substances (water between 0 ºC and 4 ºC is an exception), the coefficient of expansion is positive, so this tells us that entropy decreases with increasing pressure, and increases with decreasing pressure. The change in entropy with pressure is greatest for the vapour, so that, at lower pressures the slope of the vapour line in the graph of Gibbs function with temperature will be much steeper, and the situation will look like this:



At temperatures below A, the Gibbs function is lowest for the solid, and that is the stable phase. At temperature above A, the Gibbs function is lowest for the vapour, and that is the stable phase. At the pressure represented in the above diagram, the liquid is never the stable phase. The substance sublimates from solid to vapour as the temperature is raised.

At the pressure corresponding to the *triple point line* (remind yourself by looking at figures VI.3, VI.4 and VI.8), the diagram looks like:



At the *triple point* (A) the molar Gibbs functions of all three phases are equal, and all three phases are in equilibrium. As you increase the temperature from below A to above A, the substance sublimates directly from solid to vapour, as can also be seen from figure VI.5.

CHAPTER OVERVIEW

15: Adiabatic Demagnetization

15.1: Introduction

One way to cool a gas is as follows. First compress it isothermally. This means compress it in a vessel that isn't insulated, and wait for the gas to lose any heat that is generated so that it returns to room temperature. Then insulate the vessel and allow the gas to expand adiabatically. We could call this cooling by adiabatic decompression.

You can cool a rubber band as follows. First stretch it isothermally. That means, stretch it slowly, so that it has lots of time to lose any heat that is generated. Then, suddenly destretch it, and before it has time to gain any heat from its surrounding, measure its temperature by immediately holding it up to your lips. You will find that it has cooled by adiabatic de-stretching. (If you stretch the band quickly (i.e. adiabatically) and immediately hold it up to your lips, you will find that it is hot. **BUT ...** before you try *that* experiment, **close your eyes tightly**. You don't want the stretched elastic band to break and hit you in the eye. Believe me, you do not want that to happen.)

The method of *adiabatic demagnetization* has been used to obtain extremely low temperatures. A sample of a paramagnetic salt (such as cerium magnesium nitrate), already cooled to low temperatures by other means, is magnetized isothermally. The sample is often suspended in an atmosphere of helium, which can conduct away any heat that is produced, and hence keeps the process isothermal. It is then insulated (by pumping out the helium) and suddenly and adiabatically demagnetized. This process of isothermal magnetization followed by adiabatic demagnetization can be repeated over and over again. Temperatures close to 0 K have been reached in this manner. You could actually reach a temperature of absolute zero if you did this an infinite number of times – but not for any fewer.

In the analysis that follows, I shall have to assume that you are familiar with the concepts of **B**, **H**, magnetic moment and magnetization from electricity and magnetism.

In brief, the *magnetic dipole moment* $\mathbf{p}_m$ of a sample is the maximum torque it experiences in unit field **B**. That is, the torque is given by $\boldsymbol{\tau} = \mathbf{p}_m \times \mathbf{B}$. The magnetization **M** of a specimen is defined by $\mathbf{B} = \mu\mathbf{H} = \mu_0(\mathbf{H} + \mathbf{M})$. The magnetization is also equal to the *magnetic moment per unit volume*.

Now consider the following.

If the tension in an elastic string is F, the work done **on** the string when its length is increased by dx is $F\,dx$.

If the pressure of a gas is P, the work done **on** the gas when its volume is increased by dV is $-P\,dV$.

And the work done per unit volume **on** an isotropic sample in increasing its magnetization from M to $M + dM$ in a magnetic field B is BdM. (I am assuming here that the sample is isotropic and that the magnetic moment and the magnetic field are in the same direction, and hence I am no longer using boldface to indicate vector quantities.)

Note that, in all of these examples, the work done is the product of an intensive state variable (P, F, B) and the differential of an extensive state variable (dV, dx, dM).

If we add heat to a magnetizable sample, and do work per unit volume on it by putting it in a magnetic field B and thereby increasing its magnetization by dM, then, provided there is no change in volume, the increase in its internal energy per unit volume is given by

$$dU = TdS + BdM, \tag{15.1.1}$$

In this magnetic context, we can define state functions H, A and G per unit volume by

$$H = U - BM \tag{15.1.2}$$

$$A = U - TS \tag{15.1.3}$$

$$G = H - TS = A - BM \tag{15.1.4}$$

In differential form, these become

$$dH = TdS - MdB \tag{15.1.5}$$

$$dA = -SdT + BdM \tag{15.1.6}$$

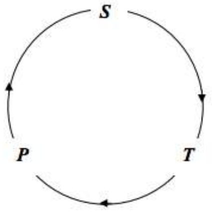
$$dG = -SdT - MdB \tag{15.1.7}$$

Here M is the dipole moment *per unit volume*, in N m T^{-1} m^{-3}, which is the same as the magnetization, in A m^{-1}. (Other equivalent units for magnetization would be Pa T^{-1} or T m H^{-1}, but I recommend N m T^{-1} m^{-3} as being the most readily understandable in the present context.)

In Section 15.2 I am going to derive an expression for the lowering of the temperature in an adiabatic decompression, $(\partial T/\partial P)_S$. And then, in Section 15.3, I am going to derive an expression, by exactly the same argument, step-by-step, for the lowering of the temperature in an adiabatic demagnetization, $(\partial T/\partial B)_S$.

15.2: Adiabatic Decompression

We are going to calculate an expression for $(\partial T/\partial P)_S$. The expression will be positive, since T and P increase together. We shall consider the entropy as a function of temperature and pressure, and, with the variables



we shall start with the cyclic relation

$$\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_S\left(\frac{\partial P}{\partial S}\right)_T=-1. \tag{15.2.1}$$

The middle term is the one we want. Let's find expressions for the first and third partial derivatives in terms of things that we can measure.

In a reversible process $dS=dQ/T$, and, in an isobaric process, $dQ=C_PdT$. Therefore

$$\left(\frac{\partial S}{\partial T}\right)_p=\frac{C_p}{T}. \tag{15.2.2}$$

Also, we have a Maxwell relation (Equation 12.6.16). $\left(\frac{\partial S}{\partial P}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_P$. Thus Equation 15.2.1 becomes

$$\left(\frac{\partial T}{\partial P}\right)_S=\frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P. \tag{15.2.3}$$

> *Check the dimensions of this. Note also that C_P can be total, specific or molar, provided that V is correspondingly total, specific or molar. $(\partial T/\partial P)_S$ is, of course, intensive.*

If the gas is an ideal gas, the equation of state is $PV=RT$, so that

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{P}=\frac{V}{T}. \tag{15.2.4}$$

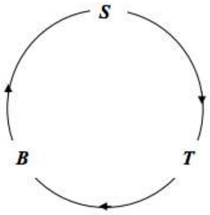
Equation 15.2.3 therefore becomes

$$\left(\frac{\partial T}{\partial P}\right)_S=\frac{V}{C_P}. \tag{15.2.5}$$

15.3: Adiabatic Demagnetization

We are now going to do the same argument for adiabatic demagnetization.

We are going to calculate an expression for $(\partial T/\partial B)_S$. The expression will be positive, since T and B increase together. We shall consider the entropy as a function of temperature and magnetic field, and, with the variables



we shall start with the cyclic relation

$$\left(\frac{\partial S}{\partial T}\right)_B \left(\frac{\partial T}{\partial B}\right)_S \left(\frac{\partial B}{\partial S}\right)_T = -1. \tag{15.3.1}$$

The middle term is the one we want. Let's find expressions for the first and third partial derivatives in terms of things that we can measure.

In a reversible process $dS = dQ/T$, and, in a constant magnetic field, $dQ = C_B dT$. Here I am taking S to mean the entropy *per unit volume*, and C_B is the heat capacity per *unit volume* (i.e. the heat required to raise the temperature of unit volume by one degree) in a constant magnetic field.

Thus we have $\left(\frac{\partial S}{\partial T}\right)_B = \frac{C_B}{T}$.

The Maxwell relation corresponding to $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ is $\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$. Thus Equation 15.3.1becomes

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C_B}\left(\frac{\partial M}{\partial T}\right)_B \tag{15.3.2}$$

.

Now for a paramagnetic material, the magnetization, for a given field, is proportional to B and it falls off inversely as the temperature (that's the *equation of state*). That is, M = *aB*/*T*. and therefore $\left(\frac{\partial M}{\partial T}\right)_B = -\frac{aB}{T^2} = -\frac{M}{T}$. Equation 15.3.2 therefore becomes

$$\left(\frac{\partial T}{\partial B}\right)_s = \frac{M}{C_B}. \tag{15.3.3}$$

You should check the dimensions of this equation.

The cooling effect is particularly effective at low temperatures, when C_B is small.

15.4: Entropy and Temperature

Cooling by adiabatic demagnetization involves successive isothermal magnetizations followed by adiabatic demagnetizations, and this suggests that some insight into the process might be obtained by following it on an entropy : temperature ($S : T$) diagram.

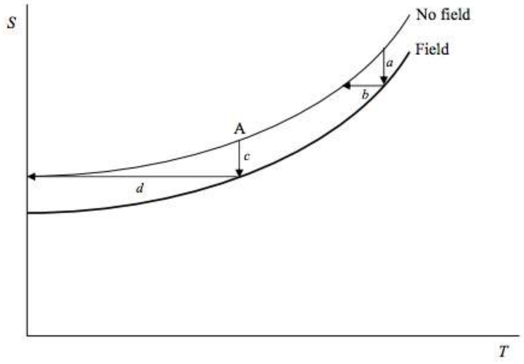


FIGURE XV.1

In figure XV.1 I draw schematically with a thin curve the variation of entropy of the specimen with temperature in the absence of a magnetizing field, and, with a thick curve, the (lesser) entropy of the more ordered state in the presence of a magnetizing field. The process *a* represents an isothermal magnetization, and the process *b* is the following adiabatic (isentropic) demagnetization, and it is readily seen how this results in a lowering of the temperature.

By the time when we reach the point A, an isothermal magnetization is represented by the process *c*, and the following adiabatic demagnetization is the process *d*, which takes us down to the absolute zero of temperature.

We shall find out in the next Chapter, however, that there is a fundamental flaw in this last argument, and that getting down to absolute zero isn't going to be quite so easy.

CHAPTER OVERVIEW

16: Nernst's Heat Theorem and the Third Law of Thermodynamics

Topic hierarchy

16.1: Nernst's Heat Theorem

At the beginning of the twentieth century, Walther Nernst (Nobel Prize in Chemistry 1920) had investigated heat capacities and heats of reaction at progressively lower temperatures. As a result of his studies, he enunciated an important principle that initially was restricted to the behaviour of reactions involving solids and liquids but which is now believed to apply to all processes and substances.

The subject of chemical thermodynamics is dealt with more fully in Chapter 17, but for the present we shall note that some chemical reactions require an input of heat to initiate them; other chemical reactions generate heat. The former are known as *endothermic* reactions; the latter are *exothermic* reactions. If the reaction takes place at constant pressure (i.e. on an open laboratory bench) the heat gained or lost is an increase or decrease in *enthalpy* H. The *heat of reaction* is usually given as ΔH, being positive for an endothermic reaction (in which the system gains heat) and negative for an exothermic reaction. It should be noted that spontaneous reactions are by no means always exothermic; some spontaneous reactions result in the absorption of heat from their surroundings and in a corresponding increase of enthalpy.

Nernst had noticed that, at progressively lower temperatures, the change in enthalpy and the change in the Gibbs function during a chemical reaction become more and more equal. And (as we shall see, what amounts to the same thing) the *rate of change of the Gibbs function with temperature* becomes less and less as the temperature is lowered. That this amounts to the same thing is evident from the Gibbs-Helmholtz relation

$$\Delta H=\Delta G-T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P. \tag{16.1.1}$$

What Nernst proposed was that, in the limit, as the temperature approaches zero, the changes in the enthalpy and Gibbs function are equal – or, what amounts to the same thing, the temperature rate of change of the Gibbs function at constant pressure approaches zero at zero temperature. And since

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P=-\Delta S, \tag{16.1.2}$$

this implies that *chemical reactions at a temperature of absolute zero take place with no change of entropy.* This is *Nernst's Heat Theorem*.

Planck later extended this to suppose that, not only does $\Delta G \to \Delta H$, but that, as $T \to 0$, the enthalpy and the Gibbs function of the system approach each other asymptotically in such a manner that, in the limit, as $T \to 0$, $G \to H$ and $(\partial G/\partial T)_P \to 0$.

This has a number of consequences. For example, until now, we had defined only what is meant by a *change in entropy*. In particular, in order to state what *the* entropy of a system is at some temperature, we would need to know what the entropy is at a temperature of zero kelvin. In Sections 12.8 and 12.9 we attempted to calculate the change in the Helmholtz and Gibbs functions as a system was changed from one state to another. We found that the right hand sides of equations 12.9.9 and 12.9.11 for calculating the changes in these functions contained the entropy. We later went on to show how we could calculate the difference in entropy in some state to that at zero temperature, but there was still a matter of an arbitrary constant, namely – what is the entropy at zero temperature? We now have the answer, resulting *from the observed behaviour of* $(\partial G/\partial T)_P$ $[= -S]$ as the temperature approaches zero – namely that the arbitrary constant is no longer arbitrary, and the entropy approaches zero as the temperature approaches zero.

Another consequence is

16.2: The Third Law of Thermodynamics

Nernst's heat theorem and Planck's extension of it, while originally derived from observing the behaviour of chemical reactions in solids and liquids, is now believed to apply quite generally to any processes, and, in view of that, it is time to reconsider our description of adiabatic demagnetization. We see immediately that figure XV.1 needs to be redrawn to reflect the fact that the entropy of the substance approaches zero whether or not it is situated in a magnetic field. The revised drawing is shown as figure XVI.1, in which I have drawn three consecutive magnetization-demagnetization operations, and it will be readily seen that we shall never reach a temperature of exactly zero in a finite number of operations.

The same applies to any operation in which we attempt to lower the temperature by a series of isothermal constraints that decrease the entropy followed by adiabatic relaxations – whether we are compressing a gas isothermally and then decompressing it adiabatically, or stretching a rubber band isothermally and loosening it adiabatically. In all cases, owing to the convergence of the two entropy curves at zero temperature, we are led to conclude:

It is impossible to reduce the temperature of a material body to the absolute zero of temperature in a finite number of operations.

This is the *Third Law of Thermodynamics*, and it is an inevitable consequence of Planck's extension of Nernst's Heat Theorem.

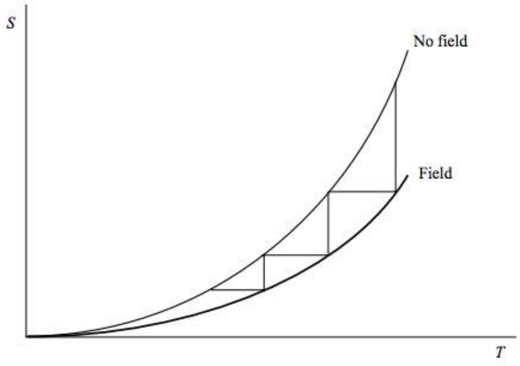


FIGURE XVI.1

This is usually taken to mean that it is impossible ever to reduce the temperature of anything to absolute zero. From a practical point of view, that may be true, though that is not strictly what the third law says. It says that it is impossible to do it in a *finite number* of operations. I cannot help but think of a bouncing ball (see Classical Mechanics Chapter V), in which the ball bounces an infinite number of times before finally coming to rest after a finite time. After every bounce, there are still an infinite number of bounces yet to come, yet it is all over in a finite time. Now, perhaps some reader of these notes one day will devise a method of performing an infinite number of isothermal stress/adiabatic relaxation operations in a finite time, and so attain absolute zero.

The third law also talks about a finite number of *operations* – by which I take it is meant operations such as an entropy-reducing constraint followed by an adiabatic relaxation. I am not sure to what extent this applies to processes such as *laser cooling*. In such experiments a laser beam is directed opposite to an atomic beam. The laser frequency is exactly equal to the frequency need to excite the atoms to their lowest excited level, and so it stops the atoms in their tracks. As the atoms slow down, the required frequency can be changed to allow for the Doppler effect. Such experiments have reduced the temperature to a fraction of a nanokelvin. These experiments do not seem to be of the sort of experiment we had in mind when developing the third law of thermodynamics. We might well ask ourselves if it is conceptually possible or impossible to reduce the speeds of a collection of atoms to zero for a finite period of time. We might argue that it is conceptually possible – but then we may remember that atoms attract each other (van der Waals forces), so, if all the atoms are instantaneously at rest, they will not remain so. Of course if we had an ideal gas (such as a real gas extrapolated to zero pressure!) such that there are no forces between the molecules, the concept of zero temperature implies that all the atoms are stationary – i.e. each has a definite position and zero momentum. This is, according the Heisenberg's uncertainty principle, inconceivable. So I leave it open as a subject for lunchtime conversations exactly how strictly the third law prevents us from ever attaining the absolute zero of temperature.

Exercise. If the kinetic temperature of a set of hydrogen atoms is reduced to a tenth of a nanokelvin, what is the root-mean-square speed of the atoms?

CHAPTER OVERVIEW

17: Chemical Thermodynamics

17.1: Equilibrium Constant

There are many types of chemical reaction, but to focus our attention we shall consider a reaction involving two reactants A and B which, when mixed, form two resultants C and D. The reaction will proceed at a certain *rate* (fast or slow), and the rate at which the reaction proceeds is part of the subject of *chemical kinetics*, which is outside the scope of this chapter, and to some extent, though by no means entirely, outside the scope of this writer! We shall not, therefore, be concerned with how fast the reaction proceeds, but with what the final state is, and whether the reaction needs some heat to get it going, or whether it proceeds spontaneously and generates heat as it does so.

We shall suppose that the reaction is *reversible*. That is, that either

$$A+B\rightarrow C+D \tag{17.1.1}$$

or

$$\mathrm{C+D\rightarrow A+B} \tag{17.1.2}$$

is possible.

That is

$$A+B\leftrightarrow C+D. \tag{17.1.3}$$

The end result is a dynamic equilibrium in which the rates of forward and backward reaction are the same, and there is an equilibrium amount of A, of B, of C and of D. The question is: How much of A? Of B? Of C? Of D?

Let us suppose that in the equilibrium mixture there are NA moles of A, N_B of B, N_C of C and N_D of D. If we make the reasonable assumption that the rate of the forward reaction is proportional to $N_\mathrm{A}N_\mathrm{B}$ and the rate of the backward reaction is proportional to $N_\mathrm{C}N_\mathrm{D}$, then, when equilibrium has been achieved and these two rates are equal, we have

$$\frac{N_A N_B}{N_C N_D}=\text{"constant"}. \tag{17.1.4}$$

The “constant”, which is called the *equilibrium constant* for the reaction, is constant only for a particular temperature; in general it is a function of temperature.

A simpler type of reaction is the dissociation-recombination equilibrium of a diatomic molecule:

$$\mathrm{AB\leftrightarrow A+B.} \tag{17.1.5}$$

The *dissociation equilibrium constant* is then

$$\frac{N_A N_B}{N_{AB}}. \tag{17.1.6}$$

This “constant” is a function of the temperature and the dissociation energy of the molecule.

A similar consideration obtains for the ionization of an atom:

$$A\leftrightarrow A^+ + e^-. \tag{17.1.7}$$

In this situation,

$$\frac{N_+N_-}{N_0}, \tag{17.1.8}$$

the *ionization equilibrium constant*, is a function of the temperature and the ionization energy. The equilibrium constants can be determined either experimentally or they can be computed from the partition functions of statistical mechanics. Some details of how to calculate the dissociation and ionization constants and how to use them to calculate the numbers of atoms, ions and molecules of various species in a hot gas are discussed in Stellar Atmospheres, Chapter 8, as well as in papers by the writer in *Publ. Dom. Astrophys. Obs.*, XIII (1) (1966) and by A. J. Sauval and the writer in *Astrophys. J. Supp.*, **56**, 193 (1984).

17.2: Heat of Reaction

In some reactions, heat is *produced* by the reaction, and such reactions are called *exothermic*. If no heat is allowed to escape from the system, the system will become hot. In other reactions, heat has to be *supplied* to cause the reaction. Such reactions are *endothermic*.

The heat of reaction is the heat required to effect the reaction, or the heat produced by the reaction – some authors use one definition, others use the other. Here we shall define the heat of reaction as the heat required *to effect* the reaction, so that it is positive for endothermic reactions and negative for exothermic reactions. (In your own writing, make sure that your meaning is unambiguous – don't assume that there is some "convention" that everyone uses.) If the reaction is carried out *at constant pressure* (i.e. on an open laboratory bench), the heat required to effect the reaction is the increase of enthalpy of the system. In other words, ΔH is positive for an endothermic reaction. If the reaction produces heat, the enthalpy decreases and ΔH is negative. Heats of reaction are generally quoted as molar quantities at a specific temperature (often 25 $^{\circ}$C) and pressure (often one atmosphere). The usual convention is to write

$$\text{A} + \text{B} \rightarrow \text{C} \ \Delta\text{H} = x \text{ J mole}^{-1}$$

One can make it yet clearer by specifying the temperature and pressure at which the enthalpy of reaction is determined, and whether the reactants are solid (s), liquid (l) or gas (g).

If the reaction is carried out *at constant volume* (in a closed vessel), the heat required to effect the reaction is the increase of the *internal energy*, ΔU. In either case, in our convention (which seems to be the most common one) ΔH or ΔU is positive for an endothermic reaction and negative for an exothermic reaction.

The heat of reaction at constant pressure (ΔH) is generally a little larger than at constant volume (ΔU), though if all reactants are liquid or solid the difference is very small indeed and often negligible within the precision to which measurements are made.

17.3: The Gibbs Phase Rule

Up to this point the thermodynamical systems that we have been considering have consisted of just a single component and, for the most part, just one phase, but we are now going to discuss systems consisting of more than one phase and more than one component. The Gibbs Phase Law provides a relation between the number of phases, the number of components and the number of degrees of freedom. But Whoa, there! We have been using several technical terms here: *Phase, Component, Degrees of Freedom*. We need to describe what these mean.

The state of a system consisting of a single component in a single phase (for example a single gas – not a mixture of different gases) can be described by three intensive state variables, P, V and T. (Here V is the molar volume – i.e. the reciprocal of the density in moles per unit volume – and is an intensive variable.) That is, the state of the system is described by a point in three-dimensional PVT space. However, the intensive state variables are connected by an *equation of state* $f(P, V, T) = 0$, so that the system is constrained to be on the two-dimensional surface described by this equation. Thus, because of the constraint, only two intensive state variables suffice to describe the state of the system. Just two of the intensive state variables can be independently varied. The system has two degrees of freedom.

Definition. A phase is a chemically homogeneous volume, solid, liquid or gas, with a boundary separating it from other phases.

Definition. The number of intensive state variables that can be varied independently without changing the number of phases in a system is called the *number of degrees of freedom* of the system.

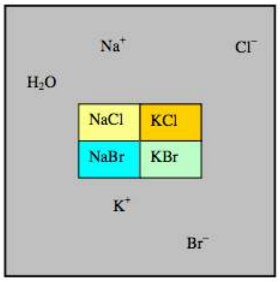
These are easy. Defining the number of *components* in a system needs a bit of care. I give a definition, but what the definition *means* can, I hope, be made a little clearer by giving a few examples.

Definition. The number of *components* in a system is the least number of constituents that are necessary to describe the composition of each phase.

Let us look at a few examples to try and grasp what this means.

First, let us consider an aqueous solution of the chlorides and bromides of sodium and potassium co-existing with the crystalline solids NaCl, KCl, NaBr, KBr, illustrated schematically in figure XVII.1.

FIGURE XVII.1



There are *five* phases – four solid and one liquid – but how many components? There are six elements: H, O, Na, K, Cl, B – but the quantities of each cannot be varied independently. There are two constraints: $n(\text{H}) = 2n(\text{O})$, and $n(\text{Na}) + n(\text{K}) = n(\text{Cl}) + n(\text{Br})$. That is, if we know the number of hydrogen atoms, then the number of oxygen atoms is known. And if we know the number of any three of Na, K, Cl or Br, then the fourth is known. Thus the number of constituents that that can be independently varied is *four*. The number of *components* is *four*.

Or again, consider an aqueous solution of a moles of H_2SO_4 in b moles of water. There is just one phase. There are *three* elements: H, O and S. These may be distributed among several species, such as H_2O, H_2SO_4, H_3O^+, OH^-, SO_4^{--}, but that doesn't matter. There is just *one* constraint, namely that

$$2(a + b)n(\text{H}) = an(\text{S}) + (4a + b)n(\text{O}) .$$

That is, if we know the number of any two of H, O or S, we also know the number of the third. The number of *components* is *two*.

Or again, consider the reversible reaction

$$CaCO_3\ (s) \leftrightarrow CaO\ (s) + CO_2\ (g) .$$

If the system is in equilibrium, and we know the numbers of any two of these *three* molecules, the number of the third is determined by the equilibrium constant. Thus the number of *components* is *two*.

In each of these three examples, it was easy to state the number of *phases* and slightly more difficult to determine the number of *components*. We now need to ask ourselves what is the number of *degrees of freedom*. This is what the Gibbs phase law is going to tell us.

If there are *C components* in a system, the composition *of a particular phase* is fully described if we know the mole fraction of C − 1 of the components, since the sum of the mole fractions of all the components must be 1. This is so for each of the *P phases*, so that there are in all $P(C-1)$ mole fractions to be specified, as well as any two of the intensive state variables P, V and T. Thus there are $P(C-1)+2$ intensive state variables to be specified. (The mole fraction of each component is an intensive state variable.) But not all of these can be independently varied, because the molar Gibbs functions of each component are the same in all phases. (To understand this important statement, re-read this argument in Chapter 14 on the Clausius-Clapeyron equation.) For each of the C components there are $P-1$ equations asserting the equality of the specific Gibbs functions in all the phases. Thus the number of intensive state variables that can be varied independently without changing the number of phases – i.e. the number of degrees of freedom, F − is $P(C-1)+2-C(P-1)$, or

$$F=C-P+2. \tag{17.3.1}$$

This is the *Gibbs Phase Rule*.

In our example of the sodium and potassium salts, in which there were $C = 4$ components distributed through $P = 5$ phases, there is just one degree of freedom. No more than one intensive state variable can be changed without changing the number of phases.

In our example of sulphuric acid, there was one phase and two components, and hence three degrees of freedom.

In the calcium carbonate system, there were three phases and two components, and hence just one degree of freedom.

If we have a pure gas, there is one phase and one component, and hence two degrees of freedom. (We can vary any two of P, V or T independently.)

If we have a liquid and its vapour in equilibrium, there are two phases and one component, and hence $F = 1$. We can vary P or T, but not both independently if the system is to remain in equilibrium. If we increase T, the pressure of the vapour that remains in equilibrium with its liquid increases. The system is constrained to lie on a line in *PVT* space.

If we have a liquid, solid and gas co-existing in equilibrium, there are three phases and one component and hence no degrees of freedom. The system exists at a single point in *PVT* space, namely the triple point.

I have often been struck by the similarity of the Gibbs phase rule to the topological relation between the number of faces F, edges E and vertices V of a solid polyhedron (with no topological holes through it). This relation is $F = E - V + 2$. E.g.

$$\begin{array}{llll} & E & V & F \\ \text{Tetrahedron:} & 6 & 4 & 4 \\ \text{Cube:} & 12 & 8 & 6 \\ \text{Octahedron:} & 12 & 6 & 8 \end{array} \tag{17.3.2}$$

As far as I know there is no conceivable connection between this and the Gibbs phase rule, and I don't even find it useful as a mnemonic. I think we just have to put it down as one of life's little curiosities.

Since writing this section, I have added some additional material on binary and ternary alloys, which provide additional examples of the Gibbs phase rule. I have added these at the end of the chapter, as sections 17.9 and 17.10.

17.4: Chemical Potential

It is a truth universally acknowledged that, if we add some heat reversibly to a closed thermodynamic system at constant volume, its internal energy will increase by $\left(\frac{\partial U}{\partial S}\right)_V dS$; or, if we allow it to expand without adding heat, its internal energy will increase by $\left(\frac{\partial U}{\partial V}\right)_S dV$. (In most cases the derivative $\left(\frac{\partial U}{\partial V}\right)_S$ is negative, so that an increase in volume results in a decrease of internal energy.) If we do both, the increase in internal energy will be

$$dU=\left(\frac{\partial U}{\partial S}\right)_V dS+\left(\frac{\partial U}{\partial V}\right)_S dV. \tag{17.4.1}$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dU=TdS-PdV. \tag{17.4.2}$$

Likewise, it is a truism that, if we add some heat reversibly to a closed thermodynamic system at constant pressure, its enthalpy will increase by $\left(\frac{\partial H}{\partial S}\right)_P dS$; or if we increase the pressure on it without adding heat, its enthalpy will increase by $\left(\frac{\partial H}{\partial P}\right)_S dP$. If we do both, the increase in internal energy will be

$$dH=\left(\frac{\partial H}{\partial S}\right)_P dS+\left(\frac{\partial H}{\partial P}\right)_S dP. \tag{17.4.3}$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dH=TdS+VdP. \tag{17.4.4}$$

Likewise, it is a truism that, if we increase the temperature of a closed thermodynamic system at constant volume, its Helmholtz function will increase by $\left(\frac{\partial A}{\partial T}\right)_V dT$; or, if we allow it to expand at constant temperature, its Helmholtz function will increase by $\left(\frac{\partial A}{\partial V}\right)_T dV$. (In most cases both of the derivatives are negative, so that an increase in temperature at constant volume, or of volume at constant temperature, results in a decrease in the Helmholtz function.) If we do both, the increase in the Helmholtz function will be

$$dA=\left(\frac{\partial A}{\partial T}\right)_V dT+\left(\frac{\partial A}{\partial V}\right)_T dV. \tag{17.4.5}$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dA=-SdT-PdV. \tag{17.4.6}$$

Likewise, it is a truism that, if we increase the temperature of a closed thermodynamic system at constant pressure, its Gibbs function will increase by $\left(\frac{\partial G}{\partial T}\right)_P dT$. (In most cases the derivative |9 \left(\frac{\partial G}{\partial T}\right)_{P}\) is negative, so that an increase in temperature at constant pressure results in a decrease in the Gibbs function.) If we increase the pressure on it at constant temperature, its Gibbs function will increase by $\left(\frac{\partial G}{\partial P}\right)_T dP$. If we do both, the increase in Gibbs function will be

$$dG=\left(\frac{\partial G}{\partial T}\right)_P dT+\left(\frac{\partial G}{\partial P}\right)_T dP. \tag{17.4.7}$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dG=-SdT+VdP. \tag{17.4.8}$$

So much, we are already familiar with. However, we can increase any of these thermodynamical functions of a system without adding any heat to it or doing any work on it – merely by adding more matter. You will notice that, in the above statements, I referred to a "closed" thermodynamical system. By a "closed" system, I mean one in which no matter is lost or gained by the system. But, if the system is not closed, adding additional matter to the system obviously increases the (total) thermodynamical functions. For example, consider a system consisting of several components. Suppose that we add dN_i moles of component i to the system at constant temperature and pressure, by how much would the Gibbs function of the system increase?

We might at first make the obvious reply: “dN_i times the molar Gibbs function of component i”. This might be true if the component were entirely inert and did not interact in any way with the other components in the system. But it is possible that the added component might well interact with other components. It might, for example, shift the equilibrium position of a reversible reaction A + B ↔ C + D. The best we can do, then, is to say merely that the increase in the (total) Gibbs function of the system would be $\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} dN_i$. Here, Nj refers to the number of moles of any component other than i.

In a similar manner, if dN_i moles of component were added at constant volume without adding any heat, the increase in the internal energy of the system would be $\left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} dN_i$. Or if dN_i moles of component were added at constant pressure without adding any heat, the increase in the enthalpy of the system would be $\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_j} dN_i$. Or if dN_i moles of component were added at constant temperature and volume, the increase in the Helmholtz function of the system would be $\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i$. If we added a little bit more of all components at constant temperature and volume, the increase in the Helmholtz function would be $\sum\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i$, where the sum is over all components.

Thus, if the system is not closed, and we have the possibility of adding or subtracting portions of one or more of the components, the formulas for the increases in the thermodynamic functions become

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_i} dV + \sum\left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} dN_i, \tag{17.4.9}$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,N_i} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N_i} dP + \sum \frac{\partial H}{\partial N_i})_{S,P,N_j} dN_i, \tag{17.4.10}$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N_i} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N_i} dV + \sum\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i, \tag{17.4.11}$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N_i} dP + \sum\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} dN_i. \tag{17.4.12}$$

The quantity $\left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j}$ is the same as $\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_j}$ or as $\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j}$ or as $\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}$, and it is called the *chemical potential* of species i, and is usually given the symbol μ_i. Its SI units are J kmole^{-1}. (We shall later refer to it as the “partial molar Gibbs function” of species i − but that is jumping slightly ahead.) If we make use of the symbol μ_i, and the other things we know from application of the first and second laws, we can write equations 17.4.9 to 17.4.12 as

$$dU = TdS - PdV + \sum \mu_i dN_i \tag{17.4.13}$$

$$dH = TdS + VdP + \sum \mu_i dN_i, \tag{17.4.14}$$

$$dA = -SdT - PdV + \sum \mu_i dN_i \tag{17.4.15}$$

and

$$dG = -SdT + VdP + \sum \mu_i dN_i \tag{17.4.16}$$

It will be clear that

$$\begin{array}{lll} \left(\frac{\partial U}{\partial S}\right)_{V,N_i} = T; & \left(\frac{\partial U}{\partial V}\right)_{S,N_i} = -P; & \left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} = \mu_i; \\ \left(\frac{\partial H}{\partial S}\right)_{P,N_i} = T; & \left(\frac{\partial H}{\partial P}\right)_{S,N_i} = V; & \left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_j} = \mu_i; \\ \left(\frac{\partial A}{\partial T}\right)_{V,N_i} = -S; & \left(\frac{\partial A}{\partial V}\right)_{T,N_i} = -P; & \left(\frac{\partial A}{\partial N_i}\right)_{V,T,N_j} = \mu_i; \\ \left(\frac{\partial G}{\partial T}\right)_{P,N_i} = -S; & \left(\frac{\partial G}{\partial P}\right)_{T,N_i} = V; & \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_j} = \mu_i. \end{array} \tag{17.4.17}$$

Since the four thermodynamical functions are functions of state, their differentials are exact and their mixed second partial derivatives are equal. Consequently we have the following twelve Maxwell relations:

$$\begin{array}{lll}
\left(\frac{\partial T}{\partial V}\right)_{S,N_i}=-\left(\frac{\partial P}{\partial S}\right)_{V,N_i}; & \left(\frac{\partial T}{\partial N_i}\right)_{S,V,N_j}=+\left(\frac{\partial \mu_i}{\partial S}\right)_{V,N_i}; & \left(\frac{\partial P}{\partial N_i}\right)_{S,V,N_j}=-\left(\frac{\partial \mu_i}{\partial V}\right)_{S,N_i}; \\
\left(\frac{\partial T}{\partial P}\right)_{S,N_i}=+\left(\frac{\partial V}{\partial S}\right)_{P,N_i}; & \left(\frac{\partial T}{\partial N_i}\right)_{S,P,N_j}=+\left(\frac{\partial \mu_i}{\partial S}\right)_{P,N_i}; & \left(\frac{\partial V}{\partial N_i}\right)_{S,P,N_j}=+\left(\frac{\partial \mu_i}{\partial P}\right)_{S,N_i}; \\
\left(\frac{\partial S}{\partial V}\right)_{T,N_i}=+\left(\frac{\partial P}{\partial T}\right)_{V,N_i}; & \left(\frac{\partial S}{\partial N_i}\right)_{T,V,N_j}=-\left(\frac{\partial \mu_i}{\partial T}\right)_{V,N_i}; & \left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j}=-\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_i}; \\
\left(\frac{\partial S}{\partial P}\right)_{T,N_i}=-\left(\frac{\partial V}{\partial T}\right)_{P,N_i}; & \left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j}=-\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_i}; & \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j}=+\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i}.
\end{array} \tag{17.4.18}$$

Refer to equations 17.4.13 to 17.4.16, and we understand that:

If we add dN_1 moles of species 1, dN_2 moles of species 2, dN_3 moles of species 3, etc., in a insulated constant-volume vessel (dS and dV both zero), the increase in the internal energy is

$$dU=\sum \mu_i dN_i. \tag{17.4.19}$$

If we do the same in an insulated vessel at constant pressure (for example, open to the atmosphere, but in a time sufficiently short so that no significant heat escapes from the system, and dS and dP are both zero), the increase in the enthalpy is

$$dH=\sum \mu_i dN_i. \tag{17.4.20}$$

If we do the same in a closed vessel (e.g. an autoclave or a pressure cooker, so that $dV = 0$) in a constant temperature water-bath ($dT = 0$), the increase in the Helmholtz function is

$$dA=\sum \mu_i dN_i. \tag{17.4.21}$$

If we do the same at constant pressure (e.g. in an open vessel on a laboratory bench, so that $dP = 0$) and kept at constant temperature (e.g. if the vessel is thin-walled and in a constant-temperature water bath, so that $dT = 0$), the increase in the Gibbs free energy is

$$dG=\sum \mu_i dN_i. \tag{17.4.22}$$

We have called the symbol μi the *chemical potential* of component *i – but in what sense is it a "potential"*? Consider two phases, α and β, in contact. The Gibbs functions of the two phases are G^α and G^β respectively, and the chemical potential of species *i* is μ_i^α in α and μ_i^β in β. Now transfer dN_i moles of *i* from α to β. The increase in the Gibbs function of the system is $\mu_i^\beta dN_i - \mu_i^\alpha dN_i$. But for a system of two phases to be in chemical equilibrium, the increase in the Gibbs function must be zero. In other words, the condition for chemical equilibrium between the two phases is that $\mu_i^\beta = \mu_i^\alpha$ for all species, just as the condition for thermal equilibrium is that $T^\alpha = T^\beta$, and the condition for mechanical equilibrium is that $P^\alpha = P^\beta$.

Students of classical mechanics may see an analogy between equation 17.4.44 and the principle of Virtual Work. One way of finding the condition of static equilibrium in a mechanical system is to imagine the system to undergo an infinitesimal change in its geometry, and then to calculate the total work done by all the forces as they are displaced by the infinitesimal geometrical alteration. If the system were initially in equilibrium, then the work done by the forces, which is an expression of the form $\sum F_i dx_i$, is zero, and this gives us the condition for mechanical equilibrium. Likewise, if a system is in chemical equilibrium, and we make infinitesimal changes dN_i, at constant temperature and pressure, in the chemical composition, the corresponding change in the Gibbs function of the system, $\sum \mu_i dNi$, is zero. At chemical equilibrium, the Gibbs function is a minimum with respect to changes in the chemical composition.

17.5: Partial and Mean Molar Quantities

Consider a single phase with several components. Suppose there are N_i moles of component i, so that the total number of moles of all species is

$$N=\sum N_i. \tag{17.5.1}$$

The *mole fraction* of species i is

$$n_i=\frac{N_i}{N}, \tag{17.5.2}$$

and of course $\sum n_i = 1$.

Let V be the volume of the phase. What will be the increase in volume of the phase if you add dN_i moles of component i at constant temperature and pressure? The answer, of course, is

$$dV=\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} dN_i \tag{17.5.3}$$

If you increase the number of moles of all species at constant temperature and pressure, the increase in volume will be

$$dV=\sum\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} dN_i. \tag{17.5.4}$$

The quantity $\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j}$ is called the *partial molar volume* of species i:

$$v_i=\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} \tag{17.5.5}$$

Let us suppose that the volume of a phase is just proportional to the number of moles of all species in the phase. It might be thought that this is always the case. It would indeed be the case if the phase contained merely a mixture of ideal gases. However, to give an example of a non-ideal case: If ethanol C_2H_5OH is mixed with water H_2O, the volume of the mixture is less than the sum of the separate volumes of water and ethanol. This is because each molecule has an electric dipole moment, and, when mixed, the molecules attract each other and pack together more closely that in the separate liquids. However, let us go back to the ideal, linear case.

In that case, if a volume V contains N moles (of all species) and you add N_i moles of species i at constant temperature and pressure, the ratio of the new volume to the old is given by

$$\frac{V+dV}{V}=\frac{N+dN_i}{N}, \tag{17.5.6}$$

and hence

$$\frac{dV}{V}=\frac{dN_i}{N}, \tag{17.5.7}$$

or

$$\left(\frac{\partial V}{\partial N_i}\right)_{P,T,N_j}=v_i=\frac{V}{N}. \tag{17.5.8}$$

Example. (You'll need to think long and carefully about the next two paragraphs fully to appreciate what are meant by *molar volume* and *partial molar volume*. You'll need to understand them before you can understand more difficult things, such as partial molar Gibbs function.)

A volume of 6 m^3 contains 1 mole of A, 2 moles of B and 3 moles of C. Thus the *molar volumes* (not the same thing as the partial molar volumes) of A, B and C are respectively 6, 3 and 2 m^3.

Assume that the mixing is *ideal*. In *that case*, equation 17.5.8 tells us that the *partial molar volume* of each is the total volume divided by the total number of moles. That is, the *partial molar volume* of each is 1 m^3. You could imagine that, before the component were mixed (or if you were to reverse the arrow of time and un-mix the mixture), we had 1 mole of A occupying 1 m^3, 2 moles of B occupying 2 m^3 and 3 moles of C occupying 3 m^3, the molar volume of each being 1 m^3.

The *mean molar volume per component* is

$$\bar{v} = \frac{V}{N}. \tag{17.5.9}$$

If the components are ideal, each component has the same partial molar volume, and hence the mean molar volume is equal to the partial molar volume of each – but this would not necessarily be the case for nonideal mixing.

The total volume of a phase, whether formed by ideal or nonideal mixing, is

$$V = \sum N_i v_i. \tag{17.5.10}$$

If you divide each side of this equation by N, you arrive at

$$\bar{v} = \sum n_i v_i. \tag{17.5.11}$$

Note that the partial molar volume of a component is not just the volume occupied by the component divided by the number of moles. I.e. the partial molar volume is not the same thing as the molar volume. In our ideal example, the molar volume of the three components would be, respectively, 6, 3 and 2 m^3.

Another way of looking at it: In the mixture, N_i moles of species i occupies the entire volume V, as indeed does every component, and its *molar volume* is V/N_i. The pressure of the mixture is P. Now remove all but species i from the mixture and then compress it so that its pressure is still P, it perforce must be compressed to a smaller volume, and the volume of a mole *now* is its *partial molar volume*.

Let Φ be any extensive quantity (such as S, V, U, H, A, G).

Establish the following notation:

Φ = total extensive quantity for the phase;

φ_i = partial molar quantity for component i;

φ = mean molar quantity per component.

The partial molar quantity φ_i for component i is defined as

$$\phi_i = \left(\frac{\partial \Phi}{\partial N_i}\right)_{P,T,N_{j*i}}. \tag{17.5.12}$$

The total value of Φ is given by

$$\Phi = \sum N_i \phi_i, \tag{17.5.13}$$

and the mean value per component is

$$\bar{\phi} = \sum n_i \phi_i. \tag{17.5.14}$$

If the extensive quantity Φ that we are considering is the Gibbs function G, then equation 17.5.12 becomes

$$g_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_{j+i}} \tag{17.5.15}$$

Then we see, by comparison with equation 17.4.28 that the *chemical potential* μ_i of component i is nothing other than its *partial molar Gibbs function*.

Note that this is not just the Gibbs function per mole of the component, any more than the partial molar volume is the same as the molar volume.

Recall (Chapter 14 on the Clausius-Clapeyron equation) that, when we had just a single component distributed in two phases (e.g. a liquid in equilibrium with its vapour), we said that the condition for thermodynamic equilibrium between the two phases was that the specific or *molar Gibbs functions* of the liquid and vapour are equal. In Section 17.5 of this chapter, when we are dealing with several components distributed between two phases, the condition for chemical equilibrium is that the *chemical potential* μ_i of component i is the same in the two phases. Now we see that the chemical potential is synonymous with the partial molar Gibbs function, so that the condition for chemical equilibrium between two phases is that the partial molar Gibbs function of each component is the same in each phase. Of course, if there is just one component, the partial molar Gibbs function is just the same as the molar Gibbs function.

Although pressure is an intensive rather than an extensive quantity, and we cannot talk of “molar pressure” or “partial molar pressure”, opportunity can be taken here to define the *partial pressure* of a component in a mixture. The partial pressure of a component is merely the contribution to the total pressure made by that component, so that the total pressure is merely

$$P=\sum p_i, \tag{17.5.16}$$

where p_i is the partial pressure of the ith component,

Dalton’s Law of Partial Pressures states that *for a mixture of ideal gases*, the partial pressure of component j is proportional *mole fraction* of component j. That is, for a mixture of ideal gases,

$$\frac{p_j}{P}=\frac{p_j}{\sum p_i}=\frac{N_j}{N}=\frac{N_j}{\sum N_i}=n_j. \tag{17.5.17}$$

That is,

$$p_j=n_jP. \tag{17.5.18}$$

17.6: The Gibbs-Duhem Relation

In a mixture of several components kept at constant temperature and pressure, the chemical potential μ_i of a particular component (which, under conditions of constant T and P, is also its partial molar Gibbs function, g_i) depends on how many moles of each species i are present. The Gibbs-Duhem relation tells us how the chemical potentials of the various components vary with composition. Thus:

We have seen that, if we keep the pressure and temperature constant, and we increase the number of moles of the components by N_1, N_2, N_3, the increase in the Gibbs function is

$$dG = \sum \mu_i dN_i. \tag{17.6.1}$$

We also pointed out in section 17.5 that, provided the temperature and pressure are constant, the chemical potential μ_i is just the partial molar Gibbs function, g_i, so that the total Gibbs function is

$$G = \sum g_i N_i = \sum \mu_i N_i, \tag{17.6.2}$$

the sum being taken over all components. On differentiation of equation 17.7.2 we obtain

$$dG = \sum \mu_i dN_i + \sum N_i d\mu_i. \tag{17.6.3}$$

Thus for any process that takes place at constant temperature and pressure, comparison of equations 17.6.1 and 17.6.3 shows that

$$\sum N_i d\mu_i = 0, \tag{17.6.4}$$

which is the *Gibbs-Duhem* relation. It tells you how the chemical potentials change with the chemical composition of a phase.

17.7: Chemical Potential, Pressure, Fugacity

Equation 12.9.11 told us how to calculate the change in the Gibbs function of a mole of an ideal gas going from one state to another. For N moles it would be

$$\Delta G = N\int C_P dT - NT_2\int C_P d(\ln T) + NRT_2\ln\left(\frac{P_2}{P_1}\right) - NS(T_2 - T_1), \tag{17.7.1}$$

where C_P and S are molar, and G is total.

Since we know now how to calculate the absolute entropy and also know that the entropy at $T = 0$ is zero, this can be written

$$G(T,P) = N(RT\ln P + \text{ constant }) \tag{17.7.2}$$

The "constant" here depends on the temperature, but is not a function of the pressure, being in fact the value of the molar Gibbs function extrapolated to the limit of zero pressure. Sometimes it is convenient to write Equation 17.7.2in the form

$$G = NRT(\ln P + \phi) \tag{17.7.3}$$

where φ is a function of temperature.

If we have a mixture of several components, the total Gibbs function is

$$G(T,P) = \sum_i N_i\,(RT\ln p_i + \text{ constant }) \tag{17.7.4}$$

We can now write this in terms of the partial molar Gibbs function of the component i – that is to say, the chemical potential of the component *i*, which is given by $\mu_i = (\partial G/\partial N_i)_{P,T,N_{j\neq 1}}$, and the *partial pressure* of component *i*. Thus we obtain

$$\mu_i = \mu_i^0(T) + RT\ln p_i \tag{17.7.5}$$

and

$$\mu_i = RT\,(\ln p_i + \phi_i) \tag{17.7.6}$$

Here I have written the "constant" as 0 μ_i^0 (T), or as $RT\varphi_i$. The constant μ_i^0 (T) is the value of the chemical potential at temperature T extrapolated to the limit of zero pressure. If the system consists of a mixture of ideal gases, the partial pressure of the *i*th component is related to the total pressure simply by *Dalton's law of partial pressures*:

$$p_i = n_i P, \tag{17.7.7}$$

where n_i is the mole fraction of the *i*th component. In that case, equation 17.7.4 becomes

$$\mu_i = \mu_i^0(T) + RT\ln n_i + RT\ln P. \tag{17.7.8}$$

and equation 17.7.5 becomes

$$\mu_i = RT\,(\ln n_i + \ln P + \phi_i)\,. \tag{17.7.9}$$

However, in a common deviation from ideality, volumes in a mixture are not simply additive, and we write equation 17.7.4 in the form

$$\mu_i = \mu_i^0(T) + RT\ln f_i, \tag{17.7.10}$$

or equation 17.7.5 in the form

$$\mu_i = RT\,(\ln f_i + \phi_i)\,. \tag{17.7.11}$$

where f_i is the *fugacity* of component *i*.

17.8: Entropy of Mixing, and Gibbs' Paradox

In Chapter 7, we defined the increase of entropy of a system by supposing that an infinitesimal quantity dQ of heat is added to it at temperature T, and that no irreversible work is done on the system. We then asserted that the increase of entropy of the system is $dS = dQ/T$. If some irreversible work is done, this has to be added to the dQ.

We also pointed out that, in an isolated system any spontaneous transfer of heat from one part to another part was likely (*very* likely!) to be from a hot region to a cooler region, and that this was likely (*very* likely!) to result in an increase of entropy of the closed system − indeed of the Universe. We considered a box divided into two parts, with a hot gas in one and a cooler gas in the other, and we discussed what was likely (*very* likely!) to happen if the wall between the parts were to be removed. We considered also the situation in which the wall were to separate two gases consisting or red molecules and blue molecules. The two situations seem to be very similar. A flow of heat is not the flow of an "imponderable fluid" called "caloric". Rather it is the mixing of two groups of molecules with initially different characteristics ("fast" and "slow", or "hot" and "cold"). In either case there is likely (*very* likely!) to be a spontaneous mixing, or increasing randomness, or increasing disorder or increasing *entropy*. Seen thus, entropy is seen as a measure of the degree of disorder. In this section we are going to calculate the increase on entropy when two different sorts of molecules become mixed, without any reference to the flow of heat. This concept of entropy as a measure of disorder will become increasingly apparent if you undertake a study of *statistical mechanics*.

Consider a box containing two gases, separated by a partition. The pressure and temperature are the same in both compartments. The left hand compartment contains N_1 moles of gas 1, and the right hand compartment contains N_2 moles of gas 2. The Gibbs function for the system is

$$G = RT\left[N_1\left(\ln P + \phi_1\right) + N_2\left(\ln P + \phi_2\right)\right]. \tag{17.8.1}$$

Now remove the partition, and wait until the gases become completely mixed, with no change in pressure or temperature. The partial molar Gibbs function of gas 1 is

$$\mu_1 = RT\left(\ln p_1 + \phi_1\right) \tag{17.8.2}$$

and the partial molar Gibbs function of gas 2 is

$$\mu_2 = RT\left(\ln p_2 + \phi_2\right). \tag{17.8.3}$$

Here the pi are the partial pressures of the two gases, given by and $p_1 = n_1P$, $p_2 = n_2P$ where the n_i are the mole fractions.

The total Gibbs function is now $N_1\mu_1 + N_2\mu_2$, or

$$G = RT\left[N_1\left(\ln n_1 + \ln P + \phi_1\right) + N_2\left(\ln n_2 + \ln P + \phi_2\right)\right]. \tag{17.8.4}$$

The new Gibbs function minus the original Gibbs function is therefore

$$\Delta G = RT\left(N_1 \ln n_1 + N_2 \ln n_2\right) = NRT\left(n_1 \ln n_1 + n_2 \ln n_2\right). \tag{17.8.5}$$

This represents a *decrease* in the Gibbs function, because the mole fractions are less than 1.

The new entropy minus the original entropy is $\Delta S = -\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$, which is

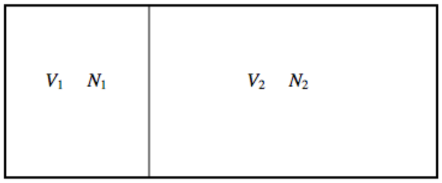
$$\Delta S = -NR\left(n_1 \ln n_1 + n_2 \ln n_2\right). \tag{17.8.6}$$

This is positive, because the mole fractions are less than 1.

Similar expressions will be obtained for the increase in entropy if we mix several gases.

Here's maybe an easier way of looking at the same thing. (Remember that, in what follows, the mixing is presumed to be ideal and the temperature and pressure are constant throughout.)

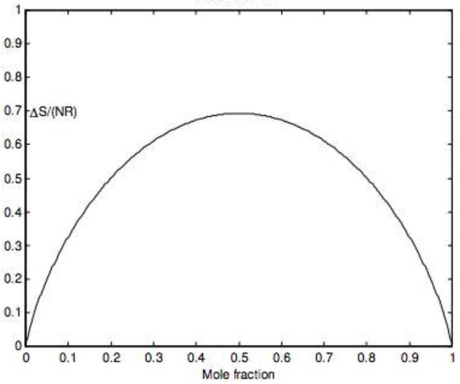
Here is the box separated by a partition:



Concentrate your attention entirely upon the left hand gas. Remove the partition. In the first nanosecond, the left hand gas expands to increase its volume by dV, its internal energy remaining unchanged ($dU = 0$). The entropy of the left hand gas therefore increases according to $dS = \frac{PdV}{T} = N_1 R \frac{dV}{V}$. By the time it has expanded to fill the whole box, its entropy has increased by ln(/). RN_1 $\ln(V/V_1)$. Likewise, the entropy of the right hand gas, in expanding from volume V_2 to V, has increased by $RN_2 \ln(V/V_2)$. Thus the entropy of the system has increased by $R[\ N_1 \ln(V/V_1) \ln(V/V_2)]$, and this is equal to $RN[\ n_1 \ln(1/n_1) \ln(1/n_2)] = -NR[n_1 \ln n_1 + n_2 \ln n_2]$.

Where there are just two gases, $n_2 = 1 - n_1$, so we can conveniently plot a graph of the increase in the entropy versus mole fraction of gas 1, and we see, unsurprisingly, that the entropy of mixing is greatest when $n_1 = n_2 = \frac{1}{2}$, when $\Delta S = NR \ln 2 = 0.6931NR$.

FIGURE XVII.1

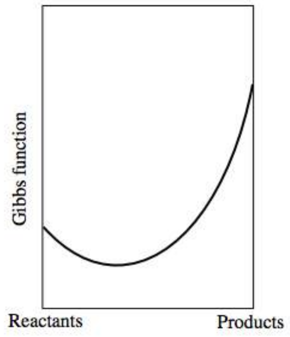


What is n_1 if $\Delta S = \frac{1}{2}NR$? (I make it $n_1 = 0.199\ 710$ or, of course, 0.800 290.)

We initially introduced the idea of entropy in Chapter 7 by saying that if a quantity of heat dQ is added to a system at temperature T, the entropy increases by $dS = dQ/T$. We later modified this by pointing out that if, in addition to adding heat, we did some irreversible work on the system, that irreversible work was in any case degraded to heat, so that the increase in entropy was then $dS = (dQ + dW_{\text{irr}})/T$. We now see that the simple act of mixing two or more gases at constant temperature results in an increase in entropy. The same applies to mixing any substances, not just gases, although the formula $-NR[n_1 \ln n_1 + n_2 \ln n_2]$ applies of course just to ideal gases. We alluded to this in Chapter 7, but we have now placed it on a quantitative basis. As time progresses, two separate gases placed together will spontaneously and probably (*very* probably!) irreversibly mix, and the entropy will increase. It is most unlikely that a mixture of two gases will spontaneously separate and thus decrease the entropy.

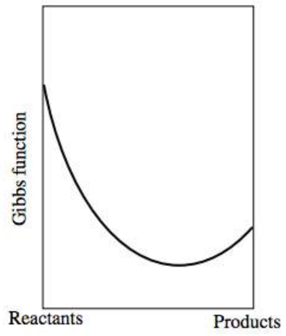
Gibbs' Paradox arises when the two gases are identical. The above analysis does nothing to distinguish between the mixing of two different gases and the mixing of two identical gases. If you have two identical gases at the same temperature and pressure in the two compartments, nothing changes when the partition is removed – so there should be no change in the entropy. Within the confines of classical thermodynamics, this remains a paradox – which is resolved in the study of *statistical mechanics*.

Now consider a reversible chemical reaction of the form Reactants ↔ Products − and it doesn't matter which we choose to call the "reactants" and which the "products". Let us suppose that the Gibbs function of a mixture consisting entirely of "reactants" and no "products" is less than the Gibbs function of a *mixture* consisting entirely of "products". The Gibbs function of a mixture of reactants and products will be less than the Gibbs function of either reactants alone or products alone. Indeed, as we go from reactants alone to products alone, the Gibbs function will look something like this:



The left hand side shows the Gibbs function of the reactants alone. The right hand side shows the Gibbs function for the products alone. The equilibrium situation occurs where the Gibbs function is a minimum.

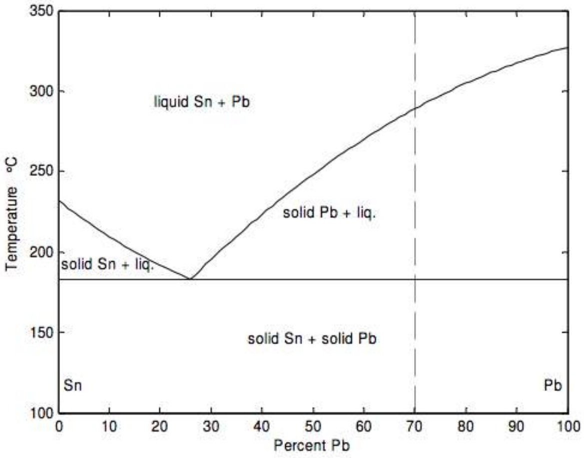
If the Gibbs function of the reactants were greater than that of the products, the graph would look something like:



17.9: Binary Alloys

(This section is a little out of order, and might be better read after Section 17.3.)

If two metals are melted together, and subsequently cooled and solidified, interesting phenomena occur. In this section we look at the way tin and lead mix. I do this in an entirely schematic and idealized way. The details are bit more complicated (and interesting!) than I present them here. For the detailed description and more exact numbers, the reader can refer to the specialized literature, such as *Constitution of Binary Alloys* by M. Hansen and K. Anderko and its subsequent Second Supplement by F. A. Shunk. In my simplified description I am assuming that when tin and lead are melted, the two liquids are completely miscible, but, when the liquid is cooled, the two metals crystallize out separately. The phenomena are illustrated schematically in the figure below, which is a graph of melting point versus composition of the alloy at a given constant pressure (one atmosphere).



The melting point of pure Pb is 327 ºC

The melting point of pure Sn is 232 ºC

In studying the diagram, let us start at the upper end of the dashed line, where the temperature is 350 ºC and we are dealing with a mixture of 70 percent Pb and 30 percent Sn (by mole – that is to say, by relative numbers of atoms, not by relative mass). If you review the definitions of phase, component, and degrees of freedom, and the Gibbs phase rule, from Section 17.3, you will agree that there is just one phase and one component (there's no need to tell me the percentage of Sn if you have already told me the percentage of Pb), and that you can vary two intensive state variables (e.g. temperature and pressure) without changing the number of phases.

Now, keeping the composition and pressure constant, let us move down the isopleth (i.e down the dashed line of constant composition). Even after the temperature is lower than 327 ºC, the mixture doesn't solidify. Nothing happens until the temperature is about 289 ºC. Below that temperature, crystals of Pb start to solidify. The full curve represents the melting point, or solidification point, of Pb as a function of the composition of the liquid. Of course, as some Pb solidifies, the composition of the liquid changes to one of a lesser percentage of Pb, and the composition of the liquid moves down the melting point curve. As long as the liquid is at a temperature and composition indicated along this curve, there is only one remaining degree of freedom (pressure). You cannot change both the temperature and the composition without changing the number of phases. As the temperature is lowered further and further, more Pb solidifies, and the composition of the liquid moves further and further along the curve to the left, until it reaches the eutectic point at a temperature of 183 ºC and a composition of 26% Pb. Below that temperature, both Pb and Sn crystallize out.

If we had started with a composition of less than 26% Pb, Sn would have started to crystallize out as soon as we had reached the left hand curve, and the composition of the liquid would move along that curve to the right until it had reached the eutectic point.

Below, we show similar (highly idealized and schematic) eutectic curves for Pb-Bi and for Bi-Sn. (For more precise descriptions, and more exact numbers, see the literature, such as the references cited above). The data for these three alloys are:

For the pure metals:

Melting point

Pb 327 ºC

Bi 271

Sn 232

Sn-Pb Eutectic 183 ºC 26% Pb

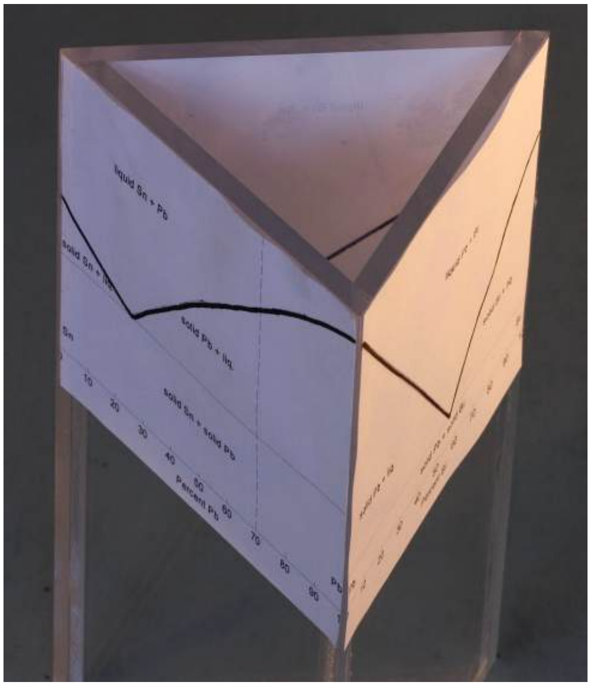
Pb-Bi Eutectic 125 ºC 56% Bi

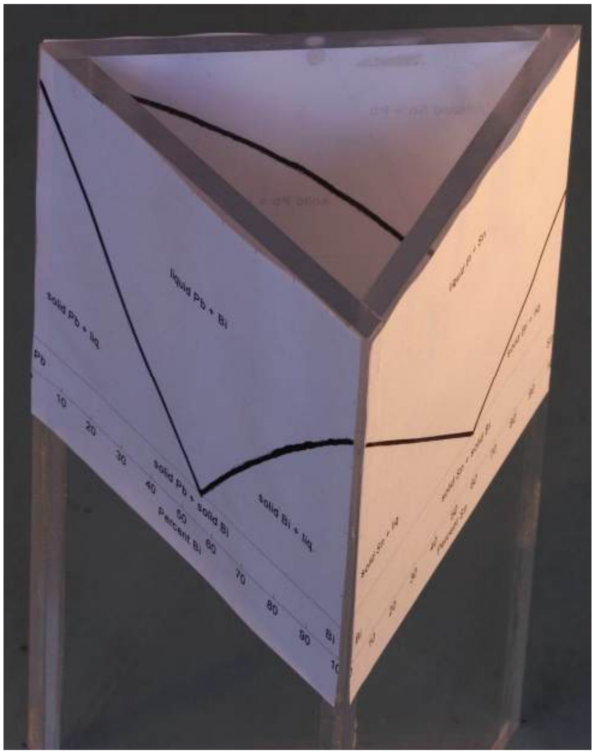
Bi-Sn Eutectic 139 ºC 57% Sn

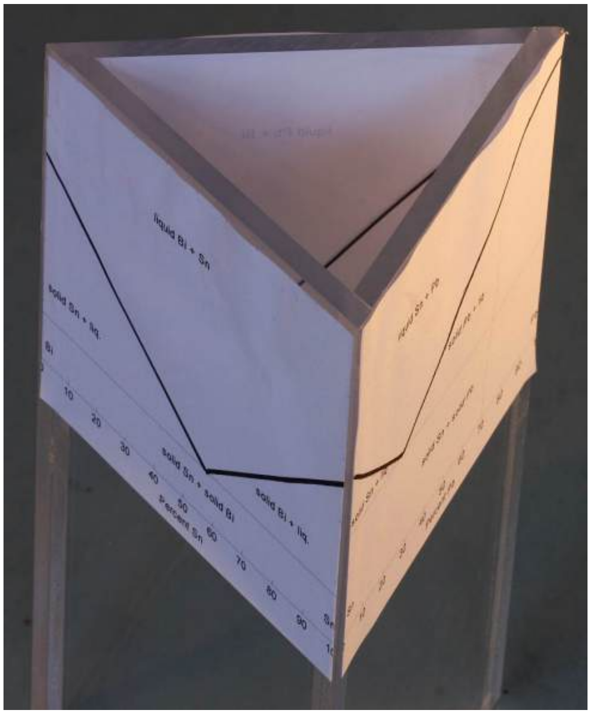
17.10: Ternary Alloys

In this section we look at what happens with an alloy of three metals, and we shall use as an example Pb-Bi-Sn. Our description is merely illustrative of the principles; for more exact details, see the specialized literature.

To illustrate the phase equilibria of an alloy of these three metals, I have pasted the eutectic diagrams of the previous section to the faces of a triangular prism, as shown below. The vertical ordinate is the temperature.

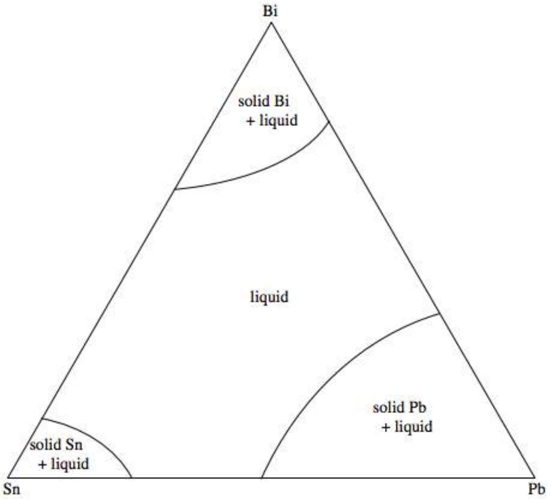






On each of the three faces only two of the metals are present. The situation where all three metals are present on comparable quantities would be illustrated by a surface inside the prism, but creating this inner surface is unfortunately beyond my skills. Anywhere above the surface outlined by the curves on each face is completely liquid. Below it one or other of the constituent metals solidifies. The surface goes down to a deep well, terminating in a eutectic temperature well below the 125 ºC of the Pb-Bi eutectic.

In lieu of building a nice three-dimensional model, the next best thing might be to take a horizontal slice through the prism at constant temperature. If I do that at, say, 200ºC, the ternary phase diagram might look something like this:



You can imagine what happens as you gradually lower the temperature. First a bit of Pb solidifies out. Then a bit of Bi. Lastly a bit of Sn. You have to try and imagine what this ternary diagram would look like as you lower the temperature. Eventually the solidification parts spread out from the corners of the triangle, and meet at a single eutectic point where there are no degrees of freedom. Below that temperature, all is solid, whatever the composition.

CHAPTER OVERVIEW

18: Experimental Measurements

Topic hierarchy

18.1: Introduction

Most of these notes on heat and thermodynamics have been largely theoretical, and almost no attention has been given to laboratory measurements of the various quantities discussed. This is not because experiment is any less important that theory. Rather it is more the consequence of my own interests and personal lack of expertise in experiment. Indeed, laboratory physics equipment has a tendency to disintegrate as soon as I approach it. However, in this chapter we shall endeavour to describe, however inadequately, some of the early classical experimental measurements.

I am under the impression that today, in order to measure *any* physical quantity, you purchase some expensive equipment, attach one end of it to the thing to be measured, and the other end to a computer, and one instantaneously obtains a digital readout of the quantity in question, without necessarily having any idea how the equipment works. And I, certainly, have little idea how much of modern high technology works. Consequently I shall restrict this chapter to brief descriptions of some of the earlier classical historical determinations of thermal quantities, many of which were performed during the nineteenth century or the early twentieth century.

Of all the many experimental determinations of physical quantities in various branches in physics, accurate determinations in the laboratory of thermal quantities are among the most difficult classical measurements of all. It would be easy to dismiss the various early experiments that I shall describe in this chapter as quaint, crude and of no modern interest. Far from it. Some of these experiments were extremely difficult to carry out accurately, and it is astonishing how accurate many of the early measurements were, as a result of the careful design, attention to detail and allowance for heat losses. The early experimenters deserve our great admiration and our gratitude for the important fundamental contributions they made to our understanding of physical science.

18.2: Thermal Conductivity

18.2.1 Solid Good Conductors (Metals)

The difference between the thermal conductivities of metals and non-metals is so large that different experimental approaches are needed for the two classes of solids, and in this subsection we deal with metals.

I remember as long ago as when I was in high school one of the experiments we had to do was to measure the conductivity of a metal rod, which, as far as I remember, was about a foot (30 cm) long and maybe two centimetres in diameter. The experiment was called Searle's Rod, or Searle's Bar, after an experimenter in the early years of the twentieth century. The experiment was simple in principle, but very difficult in practice to do accurately, and we were always advised to avoid doing heat experiments in our matriculation examinations. Heat was supplied by an electrical coil wrapped around one end the rod, and the rate of supply of heat was determined from the current through the wire and the potential difference across it, measured with an ammeter and voltmeter respectively. Heat was collected at the other end of the rod by means of a stream of water flowing through a helical tube wrapped around that end of the rod. Thermometers at the beginning and end of this helical tube measured the rise in temperature of the water. Hence one could determine the rate of flow of heat out of the cool end of the rod. If no heat were lost from side of the rod, the rate of flow of heat into the rod (determined electrically) should equal the rate of flow out of it (measured by the rise in temperature of the stream of water through the helical tube). The difference between the two would be a measure of how much heat was lost from the side of the rod. The rod was supposedly well lagged with cotton wool to keep the heat loss small. (I am talking of a high-school experiment here. One could improve on this in a more advanced laboratory by having the rod in a vacuum – so there is no loss of heat by conduction or convection, and highly polished to reduce heat loss by radiation). The temperature gradient along the length of the tube was determined by drilling pits at two points along the rod, filling these with mercury (for good thermal contact), and sticking mercury-in-glass thermometers into these little pools of mercury. One can easily imagine how difficult such an experiment was! At any rate, there was by then enough information to determine the thermal conductivity, for one knew the temperature gradient, from the thermometers stuck into the little mercury pools, and one knew the rate of flow of heat into and out of the rod, and of course one knew the cross-sectional area of the rood. In a more advanced laboratory today, rather than sticking mercury-in-glass thermometers into two mercuryfilled holes, one could measure the temperature at several points along the length of the rod by means of thermocouples or thermistors welded into the rod. If there were no heat losses along the length of the rod, the temperature gradient would be uniform along the rod. In practice, the thermistors would show a nonuniform temperature gradient, and from this one could calculate and allow for the heat loss along the rod. Likewise the temperatures at the inflow and outflow ends of the little helical tube could be measured with some tiny modern device, and all of these electrical connections today would be connected to a computer, which would immediately do all the necessary calculations, including correction of heat loss, and the thermal conductivity would be instantly displayed!

Lees developed the details of the equipment so that much smaller specimens could be used – e.g. a rod just a few cm in length and a few mm in diameter – so that he could enclose it in a Dewar flask and make measurements down to the temperature of liquid air. Three small coils of varnished copper wire were wound round the rod. (By varnished copper wire I mean copper wire whose surface was painted with a layer of varnish of sufficient thickness to insulate the coils electrically but sufficiently thin that good thermal contact with the rod was made.) One of these coils was wound round the upper end of the rod, and supplied heat at that end. The other two coils could be slid up and down to any desired positions on the rod, and they served as resistance thermometers. That is, the local temperature of the rod could be measured by measuring the resistance if the coils. This set-up provided in principle what was necessary to determine the thermal conductivity of the rod, for the rate of input of heat to the rod was determined by the current in the uppermost coil, and the temperature gradient down the rod was measured with the two movable thermometer coils.

An interesting method that has been used (using a rod of roughly the same dimensions as in Searle's Rod experiment – that is to say, about a foot (30 cm) long and one or two cm in diameter − is to pass an electrical current along length of the rod, thus heating it. However, the two ends of the rod are kept at the same temperature (T_1) by keeping them in constant-temperature baths. The temperature of the rod is greatest (T_2) at its mid-point. It can be shown, by a solution of the heat conduction equation, that

$$\sigma_{\text{therm}} = \frac{V^2}{8\left(T_2 - T_1\right)}\sigma_{\text{elect}}\,. \tag{18.2.1}$$

Here, V is the electrical potential difference, in volts, across the ends of the rod, σ_{therm} is the thermal conductivity in W m^{-1} K^{-1}, and σ_{elect} is the electrical conductivity, in S m−1 . I haven't derived that equation here (if I can, I may do so later!), but at least you can (I hope!) show that it is dimensionally correct. This method has been used to measure the ratio of the thermal to the electrical conductivity down to temperatures of a few kelvin, as well as at high temperatures.

18.2.2 Solid Poor Conductors (Non-metals)

The most obvious modification that has to be made for the measurement of the thermal conductivity of a poor conductor is in the shape of the sample to be measured. Instead of a long, thin rod, one needs a thin disc. In Lees' Discs experiment, the disc-shaped sample is clamped between two copper discs, one of which is heated with an electrical coil. The temperatures of the two copper discs are measured with thermocouples. This gives enough information, in principle, for the determination of the thermal conductivity, but, as in all thermal experiments, there are numerous refinements both for minimizing heat losses, and for allowing for what heat losses remain.

18.2.3 Liquids and Gases

Several methods have been used. Here I mention one straightforward method that has been used for both liquids and gases (i.e. fluids). The fluid is held in a long cylinder of radius b. A wire, of radius a, down the axis of the cylinder is heated electrically. The temperature T_2 of the wire can be measured by measuring its resistance, and the temperature T_1 the wall of the cylinder can be measured with a thermocouple. The rate of flow of heat $\dot{Q}$ through the fluid is equal to the rate at which electrical energy is supplied to the wire - I^2R. Anyone who has been able to work out the electric field between two coaxial cylinders in an elementary electricity course (see the Electricity and Magnetism section of these Notes) will be able to work out the relevant equations, but here goes, anyway.

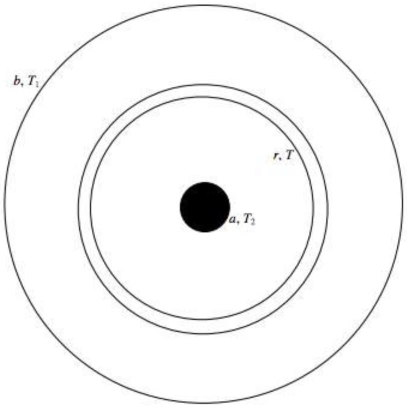
Consider an elemental cylindrical shell, radii r, $r + dr$. Its area is $2\pi rl$, where l is the length of the cylinder. If the temperature gradient there is dT/dr (which is negative), the rate of flow of heat, $\dot{Q}$ (which is known, as explained above) is given by

$$\dot{Q} = -2\pi rl\sigma\frac{dT}{dr}. \tag{18.2.2}$$

Integrate this from $r = a$, $T = T_2$ to $r = b$, $T = T_1$, and we get

$$\sigma = \frac{\dot{Q}}{2\pi l\left(T_2 - T_1\right)}\ln\left(\frac{b}{a}\right). \tag{18.2.3}$$

This assumes a very long cylinder, and ignores end effects. End effects can be kept small by using a long, thin tube, and can be allowed for by experimenting with tubes of several lengths.



18.3: The Universal Gas Constant

If you had an ideal gas, all you would have to do is to measure its pressure, its temperature, and the volume occupied by a mole, for then $PV = RT$. (Measuring P and T is relatively easy. Measuring the volume occupied by a mole is less so.) In real life, however, we have to make measurements on real gases. What has to be done is to measure the product PV (at a given temperature) at progressively lower and lower pressures, and extrapolate the value of PV/T to the limit of zero pressure. (See notes in Chapter 6 on the compression factor.)

18.4: Avogadro's Number and Boltzmann's Constant

Avogadro's number is best determined by electrolytic deposition. That is, you have to measure the quantity of electricity (current times time) that will deposit a mole of a monovalent element from an electrolytic solution on to an electrode. This quantity of electricity is generally called a *faraday*, and is about 96,484 coulombs, and is the product of the electronic charge and Avogadro's number.

Boltzmann's constant is given by $k = R/N_\text{A}$.

[It is likely that, in 2015, Avogadro’s Number and Boltzmann’s constant will be given defined values. See Section 6.1 of Chapter 6.]

18.5: Specific Heat Capacities of Solids and Liquids

In elementary instructional methods often used at high school, the method of mixtures is generally used. For example, to measure the specific heat capacity of copper, one would need a calorimeter (a small cup) made of copper, and of known mass. Pour a measured mass of boiling water (100 °C) into this. The temperature of the copper rises from room temperature, t_1 °C, to a final temperature, t_2 °C, while the temperature of the copper falls from 100 °C to t_2 °C. The specific heat capacity of the copper is then given by $m_{\text{Cu}}\, C_{\text{Cu}}\, (\text{t}_2 - \text{t}_1) = m_{\text{H2O}}\, (100 - t_2)$. Since the specific heat capacity of water is, by definition, 1 cal $\text{g}^{-1}\ \text{C}^{\circ -1}$ (at least to the precision expected at this level of experimentation), the specific heat capacity of the copper is determined.

To determine the specific heat capacity of another liquid, you could pour a measured mass of the hot liquid into the calorimeter (whose heat capacity is now known), and measure the fall in temperature of the liquid and the rise in temperature of the calorimeter, and hence deduce the specific heat capacity of the liquid by means of a similar equation to the above.

To determine the specific heat capacity of another metal, for example, iron, one can warm an iron specimen (of measured mass) to 100 °C, and then drop it into the copper calorimeter, which contains water at room temperature, t_1 °C, and then measure the final temperature t_2 °C to which the iron cools down and the copper and water heat up. Then $m_{\text{Cu}}\, C_{\text{Cu}}\, (t_2 - t_1) + m_{\text{H2O}}\, C_{\text{H2O}}\, (t_2 - t_1) = m_{\text{Fe}}\, C_{\text{Fe}}\, (100 - t_2)$.

In all such experiments, precautions must be taken to minimize heat losses, and to allow for such heat losses as remain. Most of us will remember such experiments from our schooldays, and will remember how difficult it was to get reliable results, and will be aware that there are much more accurate methods available. Furthermore, the method of mixtures measures the relative values of the specific heat capacities of the materials being mixed, rather than their absolute specific heat capacities. This is all right if we accept that the specific heat capacity of water is unity by definition, but, as soon as it is recognized that heat is a form of energy, we want to be able to measure heat capacities in joules rather than in calories, and the method of mixtures does not do this.

It must not be supposed, however, that the method of mixtures is confined to the schoolroom, and is never used in professional research laboratories. It has been found particularly useful in the measurement of heat capacities at high temperatures. While the details of such experiments are much more sophisticated than as described above, the principle of the method of mixtures still remains.

Nevertheless it remains true that the method of mixtures is really a method of comparing the specific heat capacities of different materials, or of *comparing* the specific heat capacity of a substance with that of water. The first reasonably accurate direct determination of the amount of energy needed to raise the temperature of a measured mass of water through a measured temperature rise was Joule’s famous experiment. In Joule's experiment, water was warmed by stirring it with paddles, which were operated by a set of falling weights, and the amount of work done by these falling weights could be accurately calculated in units of work (which, to Joule, were foot-pounds, but which today, we would calculate in joules.) To Joule, the object of the experiment was to demonstrate that a given amount of work always produced the same amount of heat, and hence to determine what he called the *mechanical equivalent of heat*. Today, we recognize the experiment as a direct measurement, in units of mechanical work, of the specific heat capacity of water, no longer defined to be 1 calorie per gram per degree, but measured to be 4184 joules per kilogram per kelvin. We can look back today at Joule's experiment in amazement – amazement not only at how difficult it must have been and what great experimental skills it entailed, but amazement, too, at how accurate a result he obtained. He wrote: "After reducing the result to the capacity for heat for a pound of water, it appeared that for each degree of heat evolved by the friction of water, a mechanical power equal to that which can raise a weight of 890 lbs to the height of one foot had been expended." Bearing in mind that his "degree of heat" would have been a Fahrenheit degree, this is equivalent to 4790 joules per kilogram per Celsius degree. In addition to his famous paddle-wheel experiment, Joule performed two other experiments - of a quite different nature – to determine the "mechanical equivalent of heat", and he took, as the average of the three experiments, a figure of 817 pounds, which, in modern units, would be equivalent to 4398 joules per kilogram per Celsius degree – only five percent greater than the modern value.

Of course much more accurate measurements of the energy required to raise the temperature of a solid or a liquid can be made by *heating the sample electrically* – that is, in the case of a liquid, immersing a heating coil in the liquid, or, in the case of a solid, wrapping a heating coil around the solid. Admittedly, this does not have the direct frontal approach of heating the sample by mechanical work, but at least the heat input (I^2R) can be accurately measured. Of course, as in all thermal measurements, precautions must be taken to minimize heat losses, and to allow for what heat losses remain, and these considerations must go into the detailed design of the experiment and its procedures. One technique is to surround the calorimeter by an outer vessel, which, by means of suitably-designed thermostats, is kept always at the same temperature as the calorimeter itself, thus (at least in principle) avoiding heat losses from the calorimeter altogether.

Quite precise measurements of the specific heat capacities of solids and liquids (relative to that of water) can be made with the *Bunsen Ice Calorimeter*, which is described in Section 18.7.

18.6: Specific Heat Capacities of Gases

We have to consider the measurement of the specific heat capacity at constant pressure and at constant volume.

The most famous of the early experiments to measure directly the specific heat capacity of a gas at constant pressure were Regnault's experiments of around 1860. Gas from a large storage cylinder was passed at constant pressure (measured with a manometer) through a series of helical copper tubes. The first helix was immersed in a constant high-temperature bath, which, of course, warmed the gas up. The warm gas then continued its flow through a smaller helix, which was immersed in a small copper calorimeter filled with cold water. The gas, of course, cooled down, and the water in the calorimeter warmed up. The fall in temperature of the gas and the rise in temperature of the water were measured, and hence the specific heat capacity of the gas at constant pressure was calculated. While the principle of the experiment was simple and straightforward, its actual practical execution required an experimental skill of the very highest order.

The most famous of the early experiments to measure directly the specific heat capacity of a gas at constant volume is *Joly's differential steam calorimeter* of around 1890. Two equal hollow copper spheres were suspended from the arms of a balance. One of the spheres was filled with the gas under investigation; the other was evacuated (or at least as far as the vacuum technology of the day could achieve). The two spheres were surrounded by a chamber into which steam could be pumped. I'm not very good at art, but I'll try to indicate very schematically, in figure XVIII.1, what I am trying to describe.

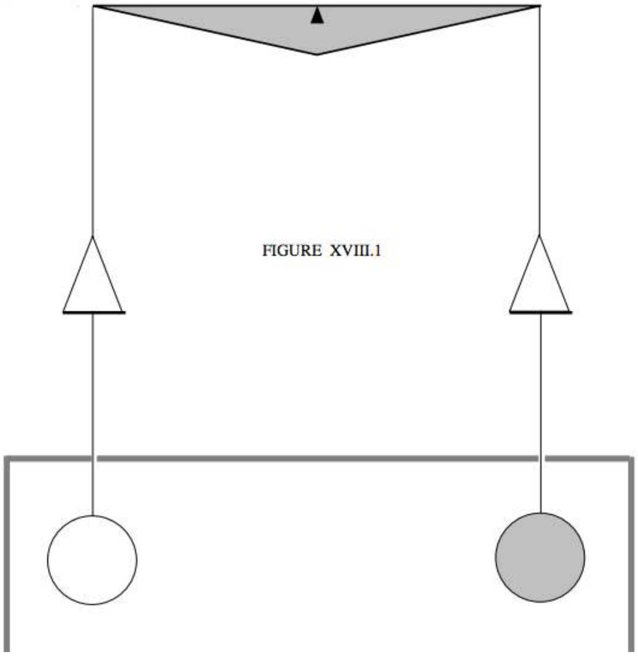


FIGURE XVIII.1

Steam was pumped into the chamber, and some of it condensed on the two spheres. Naturally, more steam condensed on the sphere that held the gas, and the mass of extra condensate was measured by adding weights to the other scale pan. The mass of extra condensate times its specific latent heat of condensation was equated to the heat required to raise the temperature of the gas inside the filled sphere from its initial room temperature to 100 °C. It was a brilliant experiment requiring superb experimental skill.

18.7: Latent Heat of Fusion

The most straightforward method for measuring the specific latent heat L of ice is to drop a lump of

Ice of mass m and specific latent heat L at its melting point T_0 into a

Calorimeter of mass MC and specific heat capacity CC and initial (warm) temperature T_2,

which contains

a mass M_W of Water of specific heat capacity C_W at the same warm temperature T_2.

After the ice has melted everything comes to a final (cool) temperature T_1. Then

$$m\left[L+C_{\mathrm{W}}\left(T_2-T_0\right)\right]=\left(M_{\mathrm{C}}C_{\mathrm{C}}+M_{\mathrm{w}}C_{\mathrm{w}}\right)\left(T_2-T_1\right). \tag{18.7.1}$$

If the temperatures in this equation are supposed to be in degrees Celsius, so that T_0 = 0, and if masses are in grams and heat in calories, so that C_2 = 1, this equation becomes

$$m\left(L+T_2\right)=\left(M_C C_C+M_W\right)\left(T_2-T_1\right). \tag{18.7.2}$$

For good results, heat losses must be minimized and allowed for, and precautions must be taken to minimize and allow for any water initially clinging to the lump of ice.

Quite precise measurements of the latent heat of fusion of ice can be made with the *Bunsen Ice Calorimeter*, an apparatus that can also be used to measure specific heat capacities of other substances. My limited artistic skills with the computer do not allow me to draw all the minute details of the practical construction of a Bunsen ice calorimeter that makes it a precision instrument, but may, perhaps, suffice to show the general principles, in figure XVIII.2. A test-tube T, is fitted with an outer glass sleeve S, the lower end of which leads to a manometer M. The portion of the sleeve above the level B is filled with air-free pure water at its freezing point. The manometer from level A to level B is filled with mercury. The entire apparatus is generally enclosed in a large ice-box, so that the entire apparatus is at 0°C. Some ice is formed outside the bottom of the test-tube, at I. In order to measure the specific latent heat of fusion of ice, a measured quantity of hot water is poured into test-tube. This water, in cooling down to 0°C, gives up a known amount of heat to the ice, some of which melts. So – how do you know how much ice has melted? Water ice contracts on melting into liquid. Consequently the level B moves up and the level A (which can be in a quite narrow capillary tube) goes down, so the reduction in volume (and hence the mass of ice melted) can be determined quite accurately. Thus the latent heat of fusion of ice can be determined. Once the equipment has been calibrated (i.e. when we know how much movement of level A corresponds to how much transfer of heat), the calorimeter can be used to measure specific heat capacities of other substances, simply by dropping a known mass of the substance at a known temperature into the test-tube, and measuring the movement of the level A. It will be understood, I think, that, in using the apparatus to measure the specific latent heat of ice, it is necessary to know the densities of ice and of water precisely. To use it for measuring the specific heat capacities of other substances, it is not necessary to know this, or even to know the specific latent heat of fusion of ice. You do have to know the specific heat capacity of water – which is not much of a burden, especially if you are content to express heat in calories!

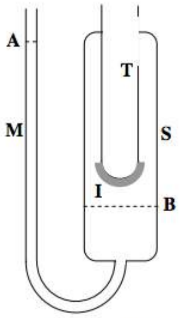


FIGURE XVIII.2

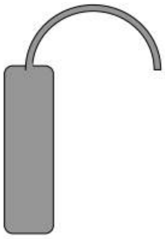
18.8: Coefficient of Expansion

If a specimen can be obtained in the form of a long rod, the simplest and most direct method is merely to rest the rod horizontally on some support, immersed in a water bath by which means the temperature can be varied. Two scratches, one at each end of the rod, can be observed with a pair of measuring microscopes held on a support at constant temperature. The measuring microscopes can either be fixed and fitted with a fine scale in the eyepiece of each, or they may be movable by means of a fine precision screw (96 turns to the inch). The movement of the microscopes can be measured either by means of a wheel fitted with a vernier that turns the precision screw, or by attaching a corner reflector to each moving microscope, and reflecting a laser beam off the reflector and counting the number of half wavelengths traversed by the microscope.

If the specimen cannot be obtained in the form of a long rod, but can be obtained in the form of a thin, flat plate with parallel faces, another method can be used. A hole might be cut in the flat specimen, and the specimen can be rested on top of a flat glass plate. A second flat glass plate rests on the upper face of the specimen. The arrangement can be illuminated with an extended monochromatic light source, to create a system of interference fringes. When the temperature is raised, the specimen expands and the distance between the glass plates increases by an amount that can be measured by measuring the movement of the interference fringes. Some materials may not be easily obtainable either in the form of a long rod or a thin plate, but perhaps they can be obtained in the form of a small cube. The specimen is placed side-by-side with a similar cube of quartz, whose expansion coefficient is very small, the two resting on the horizontal surface of a polished shiny metal or glass block. On top of the two specimens rests a thin, flat glass plate. A narrow beam of light, preferably from a laser, is directed from above to the arrangement, and two reflections are observed, one from the thin glass plate that rests on top of the specimen and its quartz companion, the other from the upper surface of the block on which the specimens are resting. When the specimen and the quartz are warmed, the specimen expands more than the quartz does, and so the upper thin glass plate tilts, and the reflection from it is deflected. The displacement of one reflected beam from the other can be measured with a microscope, and hence the tilt of the upper glass plate can be calculated, and hence the excess of expansion of the specimen over that of the quartz can be determined. The experiment gives the difference in expansion coefficient between the specimen and the quartz. The latter is very small, and its exact value need not be known with great precision in order to obtain the absolute coefficient of expansion of the specimen.

For nonvolatile liquids, a *weight thermometer* can be used. This is a glass (or, better, fused quartz) bulb fitted with a narrow capillary tube as shown in figure XVIII.3.

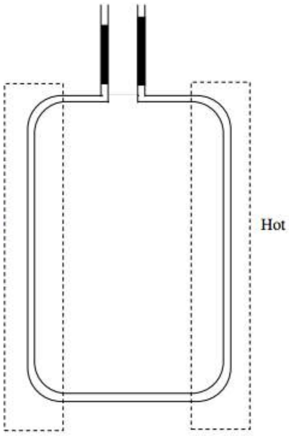
FIGURE XVIII.3



The bulb (whose weight empty is known) is completely filled (including the capillary to the very tip) with the liquid, and weighed, so that the weight, hence mass, of the liquid is known. The temperature is increased, so some liquid escapes, and the bulb is weighed again. Thus we know the weight of the liquid held by the bulb at two temperatures. If we assume that the volume is constant (the bulb being made of fused quartz) this enables us to calculate the coefficient of expansion of the liquid. Of course, the bulb does expand a little, so what we have determined is the difference between the volume expansions of the liquid and the quartz. If we know the volume expansion of the quartz (which need not be known to high precision, since it is small), we can then determine the absolute coefficient of expansion of the liquid.

In another method for measuring the coefficient of expansion of liquids, the liquid is contained in a U-tube, the two arms of which are maintained at different temperatures, as shown in figure XVIII.4. The upper ends of the two arms of the U-tube are connected to vertical tubes containing mercury for controlling and measuring the pressure. The apparatus is maintained so that the volumes of the liquids in the two arms of the U-tube are equal – but because the two arms are at different temperatures, their densities (hence specific volumes) are different, so a little extra mercury is needed to balance the hot arm against the cold arm. Thus it is possible to determine the difference in densities at the two temperatures, and hence to determine the volume coefficient of expansion. The figure shows the principle of the method; some practical refinements are needed in the actual equipment.

Figure XVIII.4



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